FEB 8 1937

UNITED STATES DEPARTMENT OF COMMERCE

Journal of Research

of the

National Bureau of Standards

Vol. 18, No. 1 January 1937

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Volume 18, Number 1
January 1937

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U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP957

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

REDETERMINATION OF THE ATOMIC WEIGHT OF ALUMINUM

By James I. Hoffman and G. E. F. Lundell

ABSTRACT

In this redetermination of the atomic weight of aluminum, weighed portions of the metal were converted to the hydroxide and sulphate, respectively. These were then heated until they were changed to the oxide, Al_2O_3, which was finally ignited at 1,200 to 1,300° C. By this procedure, the atomic weight is related directly to that of oxygen.

Careful analyses showed that the metal contained only very small quantities of impurities and disclosed no gases in the highly ignited oxide. Proper corrections were made for the small amount of impurities in the metal, and special precautions were taken to prevent absorption of moisture by the ignited oxide during weighing.

The value for the atomic weight based on this work is 26.974 ±0.002.

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I. INTRODUCTION

All recent determinations of the atomic weight of aluminum have been made by the analysis of aluminum halides,[1] [2] [3] and consequently the values depend on the purity of the halide and on the atomic

[1] T. W. Richards and H. Krepelka, J. Am. Chem. Soc. 42, 2221 (1920).
[2] H. Krepelka, J. Am. Chem. Soc. 46, 1343 (1924).
[3] H. Krepelka and N. Nikolic, Chem. Listy 19, 158 (1925), and Chem. Abs. 19, 3170 (1925).

weights of the silver and of the halogen involved. The successful determination of the atomic weight of gallium by converting the metal to the oxide [4] suggested that the atomic weight of aluminum could be similarly determined, thus directly relating it to that of oxygen and avoiding errors that might exist in determinations by less direct methods.

Previous investigators have determined the atomic weight of aluminum by converting the metal to the oxide, but the results are of doubtful value because the metal and oxide were probably impure. In 1858 Tissier [5] obtained 27.185 for the atomic weight of aluminum by converting the metal, first to the chloride, then to the nitrate, and finally to the oxide. By essentially the same method Isnard [6] obtained a value of 27. The last attempt to establish the direct ratio between aluminum and oxygen by converting the metal to the oxide was made by Kohn-Abrest [7] in 1905 when he obtained 27.23 for the atomic weight. As the above-mentioned values are in disagreement with the present accepted value,[8] and since aluminum of very high purity is now available, the present redetermination was undertaken.

II. SUITABILITY OF ALUMINUM OXIDE FOR ATOMIC-WEIGHT WORK

At the outset, it was necessary to make sure that both the metal and the oxide, Al_2O_3, are suitable for this type of work. Careful analyses, which will be discussed later, showed that the aluminum metal available was satisfactory, and it remained only to determine whether the oxide, Al_2O_3, is a suitable compound for establishing the direct ratio between aluminum and oxygen. For these tests, two portions of oxide were prepared, one by dissolving aluminum of high purity in diluted sulphuric acid, evaporating the solution to dryness and igniting the residue to the oxide, the other by dissolving the metal in diluted hydrochloric acid, precipitating with ammonium hydroxide, filtering, and igniting the precipitate to the oxide. Both portions of oxide were ignited between 1,250 and 1,300° C for 20 hours, after which they were placed in a desiccator, to be used in the tests that follow.

T. W. Richards and E. F. Rogers [9] found that many oxides contained gases (chiefly oxygen and nitrogen) which they did not succeed in driving out by heating in a vacuum or by heating with a blast lamp. Our work on gallic oxide [10] indicated that prolonged ignition at 1,200 to 1,300° C tends to free gallic oxide from tightly held gases. Aluminum oxide, formed in the same way, could reasonably be expected to be free from gases. To test this, samples of both portions of the prepared oxides were analyzed for their gas content by a procedure similar to that described in the paper just cited. For this purpose, a modification of the ordinary tubulated Gooch crucible was designed so that the aluminum oxide could be fused with borax at 1,000 to 1,100° C without any danger of softening the cement that was used to seal the cover on the crucible. This water-jacketed Gooch crucible is shown in figure 1.

[4] G. E. F. Lundell and James I. Hoffman, J. Research NBS 15, 409 (1935) RP838.
[5] Ch. Tissier, Compt. rend. 46, 1105 (1858).
[6] Note in Compt. rend. 66, 508 (1868).
[7] Emile Kohn-Abrest, Bul. soc. chim. [3] 33, 121 (1905).
[8] J. Am. Chem. Soc. 48, 541 (1926), and 58, 541 (1936).
[9] Proc. Am. Acad. Arts Sci. 28, 200 (1893).
[10] J. Research NBS 15, 409 (1935) RP838.

A 6-g portion of borax, $Na_2B_4O_7.10H_2O$, was heated in the open crucible until water and visible bubbles of gas were expelled. By means of Cementyte a small glass cap was sealed over the end of tube *B;* then the cover was sealed to the crucible, and tube *A* to a manometer. The fused borax was then heated for 3 hours at about 1,000° C in a vacuum. After cooling, the cover was removed, 1 g of the highly ignited aluminum oxide was quickly placed on top of the borax, and the cover was again sealed in place. After evacuating the system (having a total volume of about 45 ml), the borax and aluminum oxide were heated at 1,000 to 1,100° C for 40 to 60 minutes. In this time practically all the aluminum oxide was dissolved in the borax. When the system had cooled to the original temperature, the change in pressure was noted and compared with the change obtained in a blank determination involving only the borax. In a series of 10 determinations, including samples from both portions of oxide, the average difference between the blanks and the determinations involving 1 g of oxide was equivalent to less than 0.1 ml of gas, as calculated from the volume of the system and the difference in pressure before and after the fusions (1 mm of Hg being equivalent to approximately 0.06 ml). In checking this procedure, 0.43 and 0.60 ml of gas were obtained, respectively, from 0.5-g portions of zinc oxide which was shown to contain 0.96 ml of gas per gram. The amount of gas in the zinc oxide was determined by dissolving the oxide in diluted hydrochloric acid [11] (1+4) and collecting the gas in a graduated tube. Some of the cooled melts resulting from the fusion of the aluminum oxide in borax were also dissolved in diluted hydrochloric acid (1+4), but no gas was obtained. As a whole, the blanks were high and the results obtained in the determination of gases did not check as well as might be desired, but it can be stated definitely that no significant quantity of gas was contained in the aluminum oxide which had been ignited for 20 hours or more at 1,200 to 1,300° C.

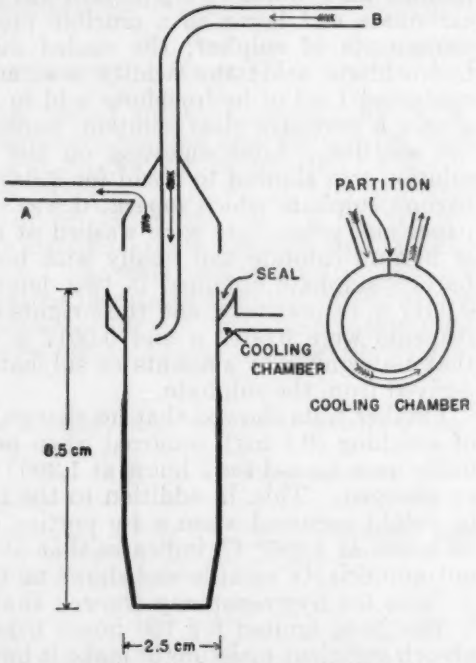

FIGURE 1.—*Water-jacketed tubulated Gooch crucible.*

The crucible is made of platinum containing 3.5 percent of rhodium and is of extra thickness in the lower part to prevent distortion during fusions.

As it is known to be difficult to obtain constant weight by igniting aluminum hydroxide to the oxide, tests for small quantities of water

[11] Diluted hydrochloric acid means the concentrated reagent to which an indefinite volume of water has been added. Diluted hydrochloric acid (1+4) denotes 1 volume of concentrated hydrochloric acid (sp gr 1.18) diluted with 4 volumes of water. If no dilution is specified, the concentrated reagent is meant. This system of specifying diluted acids is used throughout this paper.

in the final ignited product seemed desirable. The oxide which was derived from the hydroxide did not yield any gas during fusion with borax in a vacuum. This alone was probably sufficient evidence to show that no appreciable amount of water was retained, but it was deemed advisable to add some substance containing a known amount of moisture and then fuse the mixture with borax in a vacuum. One milligram of bauxite containing 0.27 mg of water was accordingly added to 1 g of the highly ignited aluminum oxide, and the mixture was fused. After cooling to the original temperature, the manometer reading definitely showed an increase in pressure and indicated 0.25 mg of water. This shows that a small amount of water would have been revealed by the fusion in a vacuum if it had been present.

To test for residual sulphate in the oxide that was formed by igniting the sulphate, a 2-g portion was fused with a mixture of sodium carbonate and borax in a crucible protected from gases containing compounds of sulphur; the cooled melt was dissolved in diluted hydrochloric acid; the acidity was adjusted so that the solution contained 1 ml of hydrochloric acid in 100 ml, and, after filtering to obtain a perfectly clear solution, barium chloride was added to the hot solution. After digesting on the steam bath for 1 hour, the solution was allowed to stand for 2 days at room temperature. The barium sulphate which separated was collected on a small filter, the paper and precipitate were washed at first with a 1-percent solution of barium chloride and finally with hot water. The weights of the barium sulphate obtained in two determinations were 0.0016 g and 0.0017 g, respectively, and the weights obtained in two blanks on the reagents were 0.0017 g and 0.0017 g, respectively, which indicates that no significant amounts of sulphate were retained by the oxide derived from the sulphate.

Further tests showed that no change, within the limits of accuracy of weighing (0.1 mg), occurred when portions of the strongly ignited oxide were heated for 2 hours at 1,300° C in an atmosphere of oxygen or nitrogen. This, in addition to the fact that no detectable change in weight occurred when a 4-g portion of oxide was heated in air for 50 hours at 1,300° C, indicates that at this temperature the oxide is not appreciably volatile and shows no tendency to dissociate.

Tests for hygroscopicity showed that aluminum oxide, even after it has been ignited for 100 hours between 1,200 and 1,300° C, will absorb sufficient moisture to make it impossible to weigh it accurately in a container that is open to the atmosphere. For example, an 8-g portion of the strongly ignited oxide absorbed 0.0113 g of moisture when it was exposed in an open platinum crucible for 2 hours in an atmosphere having a relative humidity of 80 percent. Three additional days of exposure, however, caused practically no further change in weight. The troubles caused by hygroscopicity were overcome by transferring the crucibles directly from the furnace to a Pyrex glass weighing bottle shown in figure 2, and described in a later section.

By taking into consideration (1) that aluminum oxide that has been derived from the hydroxide or sulphate and has been ignited for 20 hours or more at 1,200 to 1,300° C contains no appreciable amount of gas, (2) that the oxide shows great stability under varying conditions, (3) that the oxide derived from the hydroxide retains no significant quantity of water, (4) that the oxide derived from the sulphate

contains no significant quantity of residual sulphate, and (5) that the difficulties caused by hygroscopicity can be overcome by a special type of weighing bottle, it was concluded that this oxide, Al_2O_3, ignited at 1,300° C, is a suitable compound to use in determining the atomic weight of aluminum.

III. ANALYSIS OF THE ALUMINUM METAL

Two lots of aluminum were used in this work. The purer lot was furnished in the form of notch-bars through the courtesy of H. V. Churchill and R. W. Bridges, Chief Chemist and Assistant Chief Chemist, respectively, of Aluminum Research Laboratories, Aluminum Co. of America, New Kensington, Pa. In the discussion which follows, this lot will be referred to as aluminum *A*. The other lot is the standard sample 44c, furnished by the National Bureau of Standards as a melting-point standard.

1. SPECTROCHEMICAL ANALYSIS

Samples from both lots were tested spectrochemically by B. F. Scribner of the Bureau's Spectroscopy Section, and the spectra were examined for the sensitive lines of Ag, As, Au, B, Be, Bi, C, Ca, Cb, Cd, Ce, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Sc, Si, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. The elements, other than aluminum, that were detected are listed in table 1. The scale used by the Spectroscopy Section in qualitatively designating increasing amounts of impurities is: *trace*, *very weak*, *weak*, *moderate*, and *strong*. The designation *faint trace* is used only when the most sensitive lines of the impurity appear near the limit of visibility.

TABLE 1.—*Results of chemical and spectrochemical analyses of aluminum metal*

Elements found or for which special tests were made	Aluminum *A*		Aluminum sample 44c	
	Chemical determination (figures are expressed in percent)	Qualitative spectrochemical designation [1]	Chemical determination (figures are expressed in percent)	Qualitative spectrochemical designation
B	Not detected [2]	Not detected	Not detected	Not determined.
Be	do	do	do	Not detected.
C	do	do	do	Do.
Ca	Not determined [3]	do	do	Faint trace.
Cr	Not detected	do	do	Do.
Cu	0.002	Trace	0.006	Trace.
Fe	0.003	do	0.007	Do.
Ga	([4])	Faint trace	0.0004	Faint trace.
Mg	Not detected	Trace	Not detected	Trace.
Mn	<0.0002	Faint trace	do	Faint trace.
Mo	([4])	Not detected	0.00002	Not detected.
Na	Not determined	Faint trace	Not determined	Faint trace.
Pb	Not detected	Not detected	Not detected	Do.
P	<0.001	Not determined	do	Not determined.
S	Not detected	do	0.0001	Do.
Si	0.006	Trace	0.011	Trace.
Ti	([4])	Faint trace	0.0001	Not detected.
V	([4])	Not detected	Not detected	Do.
Zr	([4])	do	0.0003	Do.

[1] The same qualitative spectrochemical designation is given for iron and for gallium in both lots of metal, but the lines indicated that standard sample 44c contains more iron and gallium than aluminum *A*.
[2] "Not detected" means that the material was examined, but the element was not found.
[3] "Not determined" means that the material was not examined for the element.
[4] See (b) and (c) under Chemical Analysis in text, page 5 ,6 and 7.

2. CHEMICAL ANALYSIS

For most of the determinations, the conventional methods of analysis were used. The careful analysis of sample 44c was made by J. A. Scherrer, who determined gallium and most of the other impurities by the methods described or suggested in *Determination of Gallium in Aluminum*.[12] Aluminum *A* was analyzed by one of the authors. Details will be given only in those cases in which the determinations seem to be of especial interest, or in which unexpected difficulties were encountered. Careful blank determinations in duplicate were made on the reagents in all the following tests.

(a) SILICON

A 10-g sample of aluminum A was transferred to a 600-ml Pyrex beaker and dissolved in 500 ml of a mixture of acids prepared by mixing 485 ml of water, 115 ml of sulphuric acid, 200 ml of hydrochloric acid, and 200 ml of nitric acid. The beaker was immersed in ice water to retard the reaction. The solution was evaporated until fumes of sulphuric acid appeared. Warm water was then added to the partially cooled residue, and the beaker was placed on the steam bath until the aluminum sulphate was dissolved. The solution was poured through a small filter, the paper was washed with hot water, and the filtrate and washings were again evaporated until fumes of sulphuric acid appeared. After the aluminum sulphate was dissolved, the solution was poured through a small filter, the paper was washed with hot water, and the silicon in the two papers was determined in the usual manner by igniting the papers, weighing the residue, then treating it with hydrofluoric and sulphuric acids, and again igniting and weighing. The small nonvolatile residue that remained after the silica was volatilized was fused with a small quantity of sodium carbonate, the cooled melt was dissolved in diluted hydrochloric acid, and the resulting solution was evaporated to dryness. The dried residue was treated with 20 ml of diluted hydrochloric acid (1+20), and the solution was examined for silica. None was found, which indicates that all the silicon was oxidized by the mixture of acids, and that no silicon remained in the nonvolatile residue.

(b) ELEMENTS THAT ARE PRECIPITATED BY HYDROGEN SULPHIDE IN ACID SOLUTION (COPPER)

A 100-g sample of aluminum *A* was dissolved in a slight excess of diluted hydrochloric acid (1+2). The resulting solution was diluted to 2 liters, and the acidity was adjusted so that about 2 percent by volume of hydrochloric acid was present. The solution was heated nearly to boiling, and a rapid stream of hydrogen sulphide was passed into it for 3 hours while it cooled. After standing overnight, the small precipitate which formed was collected on a filter. The paper and precipitate were decomposed in a mixture of nitric and sulphuric acids, and nitric acid was expelled by evaporating until fumes of sulphuric acid appeared. The cooled solution was diluted with water and filtered to remove any silica that might have separated. The acidity of the filtrate was adjusted to 2 percent by volume, and the

[12] J. A. Scherrer, J. Research NBS 15, 585 (1935) RP853.

precipitation with hydrogen sulphide was repeated. The resulting precipitate was collected on a filter, ignited at 500° C in a porcelain crucible, cooled, and weighed. The residue weighed 0.0027 g. This was dissolved in nitric acid, and the copper in it was determined colorimetrically.[13] The determination indicated 0.00175 g of copper, equivalent to 0.0022 g of CuO. This leaves only the difference between 0.0027 g and 0.0022 g or 0.0005 g of oxides to be distributed among all the other elements that are precipitated by hydrogen sulphide in acid solution. Since 0.0005 g in a 100-g sample is without significance in this work, no attempt was made to separate this small weight of oxides into its constituents.

(c) ELEMENTS THAT ARE PRECIPITATED BY CUPFERRON (IRON)

Iron, vanadium, titanium, zirconium, tin, and gallium are completely precipitated by cupferron in a solution containing 5 ml of sulphuric acid in 100 ml. It was therefore decided to precipitate all these elements and to determine their composite weight in the form of oxides. Filtrates from the silicon determinations were combined so that the solution contained the equivalent of 21.0 g of aluminum in a volume of 1 liter. The acidity was adjusted to 5 ml of sulphuric acid in 100 ml, the solution was cooled, and an excess of cupferron was added. After standing in ice water for 3 hours, the precipitate was collected on a filter and washed with cold diluted sulphuric acid (1+100) containing a little cupferron. The paper and precipitate were decomposed by digestion with nitric and sulphuric acids, and the nitric acid was expelled by evaporating until fumes of sulphuric acid appeared. After cooling, 100 ml of water was added, and the acidity was adjusted so that the solution contained 5 ml of sulphuric acid. The precipitation with cupferron was repeated, and the precipitate was collected on a filter, ignited in platinum, treated with hydrofluoric and sulphuric acids, again ignited, and weighed. The weight of the residue was 0.0011 g. Iron oxide in this residue was determined by leaching the oxides with hydrochloric acid and applying the colorimetric method of Stokes and Cain [14] to the solution. Iron, equivalent to 0.0009 g of Fe_2O_3 was found. Since this left only 0.0002 g to be distributed among all the other oxides of the elements that are precipitated by cupferron, and since such a small weight, compared with the weight of sample taken, is without significance in this work, no further efforts were made to determine the constituents of the residue. Qualitative tests showed it to be free from copper.

The percentage of iron, as calculated from the quantity found by the above procedure, is 0.003. By cutting out little pieces, such as were used in the atomic weight determinations, dissolving them in diluted hydrochloric acid, and applying the colorimetric method of Stokes and Cain, 0.0027 percent of iron was found. This shows that no significant amount of iron was introduced by the tools used in preparing the samples for the atomic weight determination.

(d) MAGNESIUM

A 14-g sample of aluminum was placed in a Pyrex beaker containing 500 ml of cold water, and 25-ml portions of a 30-percent solution of sodium hydroxide were added at intervals until the alumi-

[13] See G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 274 (J. Wiley and Sons, New York, N. Y., 1931).
[14] H. N. Stokes and J. R. Cain, Bul. BS 3, 115 (1907) 853.

num was dissolved. The solution was then heated on the steambath for 1 hour, cooled to room temperature, and filtered. After washing the precipitate with a 1-percent solution of sodium hydroxide, it was dissolved in diluted hydrochloric acid, 1 g of citric acid was added to the solution, and the magnesium was determined by the usual procedure of twice precipitating with diammonium phosphate and igniting the precipitate to the pyrophosphate, $Mg_2P_2O_7$. The weights of $Mg_2P_2O_7$ obtained in two determinations were the same as that obtained in a blank determination involving only the reagents. As a check on the method, 0.0014 g of magnesium powder was added to one blank at the start. After allowing for the blank on the reagents, the weight of $Mg_2P_2O_7$ obtained (0.0064 g) corresponded exactly to the weight of magnesium added. These tests indicate that if magnesium is present, the amount is entirely negligible.

(e) MANGANESE

A 10-g sample was dissolved in diluted hydrochloric acid (1+1), 50 ml of sulphuric acid was added, and the hydrochloric acid was expelled by heating until fumes of sulphuric acid appeared. The cooled residue was dissolved in water, then nitric and phosphoric acids were added, and the solution was boiled with potassium periodate.[15] A barely visible pink color appeared which was estimated colorimetrically to amount to less than 0.0002 percent of manganese.

(f) BERYLLIUM

A 20-g sample of aluminum *A* was dissolved in diluted hydrochloric acid (1+1), and after the volume was adjusted to 600 ml, the solution was cooled to about 5° C and saturated with hydrochloric acid gas. The bulk of the aluminum was precipitated as the hydrated chloride, $AlCl_3.6H_2O$, and removed by filtration.[16] The precipitate was washed with cold hydrochloric acid saturated with hydrochloric acid gas. The filtrate and washings were concentrated to a volume of 20 ml, the solution was cooled, an equal volume of ether was added, and then the solution was saturated with hydrochloric acid gas. The small precipitate of hydrated aluminum chloride was removed by filtration and washed with a cold solution prepared by mixing equal volumes of hydrochloric acid and ether and saturating it with hydrochloric acid gas.

The filtrate and washings were evaporated to dryness, the residue was dissolved in diluted hydrochloric acid, and the iron and the small quantity of aluminum that might have remained in the solution [17] were precipitated by 8-hydroxyquinoline from an acetic acid solution, buffered with ammonium acetate (pH of approximately 6.8). The procedure described by Knowles for the separation of beryllium from aluminum was followed.[18] The filtrate was evaporated with nitric, sulphuric, and perchloric acids to destroy the excess of 8-hydroxyquinoline. When the reagent was destroyed, 50 ml of water was added and the solution was rendered slightly ammoniacal. After standing for 4 hours, a precipitate appeared which, after ignition,

[15] See G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 199 (J. Wiley and Sons, New York, N. Y., 1931).
[16] See F. A. Gooch and F. S. Havens, Am. J. Sci. [4] 2, 416 (1896).
[17] The precipitate was very small and appeared to be mostly iron, which indicates that the aluminum was practically quantitatively precipitated by the treatment with hydrochloric acid and ether.
[18] H. B. Knowles, J. Research NBS 15, 87 (1935) RP813.

weighed 0.2 mg more than that obtained in a blank carried through all the steps of the method. Although this weight is insignificant, the ignited residue was subjected to spectrochemical analyses by B. F. Scribner. No beryllium was detected, but faint traces of vanadium, bismuth, and titanium were indicated, which may have accounted for the 0.2-mg excess in the weight of the residue.

(g) NITROGEN

A 10-g sample of the metal was dissolved in diluted hydrochloric acid (1+1) in a flask fitted with a trap to prevent access of ammonia from the air. After solution was complete, the trap was removed, a funnel was placed in the neck of the flask, and a 30-percent solution of sodium hydroxide was poured in until the solution was strongly alkaline. A moist piece of red litmus paper was then pinched between the funnel and the inner surface of the mouth of the flask. The red litmus did not turn blue during 3 hours of heating on the steam bath. In a similar determination in which 0.4 mg of ammonium chloride, equivalent to 0.1 mg of nitrogen, had been added to the solution, the red litmus had turned blue at the end of 15 minutes. This indicates that if nitrogen is present as the nitride, its amount is less than 0.02 mg in a 2-g sample, which is entirely negligible.

(h) OCCLUDED GASES

A small piece of aluminum, weighing 5.0 g, was fused in a vacuum in the apparatus used for determining gases in the oxide. A small porcelain crucible was used as the container for the metal inside of the tubulated Gooch crucible to prevent the aluminum from coming in contact with the platinum. The manometer showed a slight increase in pressure, but this did not differ by more than 1 mm of Hg from that obtained when the porcelain crucible alone was heated in the apparatus in a blank determination. This indicates that 5.0 g of the metal contained less than 0.1 mg of occluded gases.

(i) CARBON

Aluminum shavings, such as are obtained in the usual sampling operations, do not burn rapidly in air or oxygen even at a temperature of 1,300° C. The coating of oxide that forms on the surface prevents burning of the metal within, and heating at 1,300° C. in oxygen for as much as 4 or 5 hours usually does not effect complete oxidation of the metal. It is obvious that an accelerator or flux must be used. Various substances were tried, but only one, copper oxide, was found to be satisfactory.

In the procedure finally used, the aluminum shavings were burned in the type of furnace used in the determination of carbon in steel.[19] Because of the high temperature required, the type that is heated by silicon carbide elements was used. A nickel boat, previously ignited in oxygen, was filled with 90-mesh alundum, and then 1 g of aluminum shavings was placed in a groove in the alundum. After distributing the aluminum uniformly throughout the length (10 cm) of the boat, 0.5 g of copper oxide, CuO, was evenly distributed on top of the metal. A nickel cover was placed over the boat, and the charge was put in the combustion tube which had previously been heated to 1,000° C. As

[19] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 154-18[7] (J. Wiley and Sons, New York, N. Y., 1931).

soon as the tube was closed, a rapid stream of oxygen was admitted, and the temperature of the furnace was raised from 1,000 to 1,325 ± 25° C, within 20 minutes. The latter temperature was maintained for one-half hour. The gases issuing from the furnace were passed through a tube containing platinized silica gel designed to remove compounds of sulphur, and then through a small tube containing Ascarite (sodium hydroxide on asbestos). The exit-end of the absorption tube contained anhydrous magnesium perchlorate, and a guard tube containing Ascarite and anhydrous magnesium perchlorate was attached to prevent moisture or carbon dioxide from the air from entering the absorption tube in case of back pressure which might result from rapid combustion of the aluminum.

By this procedure the aluminum was fairly completely burned, but occasionally a little of the metal remained in places where the slag ran together into rather thick nodules. Judging by the amount of hydrogen that was evolved when the pulverized slag was treated with hydrochloric acid, all but 1 or 2 percent of the metal was burned in every case. In the case of aluminum A, the average increase in weight of the absorption tube in four blank determinations was the same as in four determinations when aluminum was being burned. This indicates that there is no carbon in this material. In the case of aluminum sample 44c, there was a slight indication of the presence of carbon, but calculations showed that the amount could not have been greater than 0.003 percent. Tests of the method were made by adding chips of steel, containing carbon equivalent to 0.4 mg of carbon dioxide, to the chips of aluminum. The amount of carbon added was recovered in every case. Spectrochemical tests failed to show carbon in either of the two materials, but the sensitivity of the spectrochemical test is not known in the case of carbon.

(j) ALUMINUM OXIDE (Al_2O_3)

Metallic aluminum is said to contain small quantities of oxide [20] which may have been formed in the process of melting and pouring, or as a thin surface film by exposure to the atmosphere. In this work the total amount of aluminum oxide was determined by analyzing the residue left when the metal was subjected to a stream of dry hydrochloric acid gas and hydrogen at temperatures between 400 and 600°C. In general, the procedure described by Withey and Millar was used. Under these conditions metallic aluminum reacts to form the anhydrous chloride which is volatilized, while any aluminum oxide remains as a nonvolatile residue. In order to prevent oxidation of the metal, it was found that all air and moisture had to be displaced from the apparatus by passing a rapid stream of dry hydrogen through it for 4 to 6 hours before the metal was heated. In all determinations the hydrogen was purified by passing it over hot copper gauze and then through Ascarite (sodium hydroxide on asbestos) followed by anhydrous magnesium perchlorate. The hydrochloric acid gas was passed through a tower of anhydrous calcium chloride and then through anhydrous magnesium perchlorate.

Pieces of aluminum, weighing from 2 to 3 g and having a surface area of 6 to 8 cm^2 were cut out of an ingot with a sharp chisel. The

[20] Hirsch Löwenstein, Z. anorg. allgem. Chem. **199**, 48 (1931), reported 0.008 percent as the normal content of the Al_2O_3 in new aluminum metal. W. H. Withey and H. E. Millar, J. Soc. Chem. Ind., Trans. (London) **45**, 170 (1926), found as much as 0.066 percent in thin sheets.

surfaces of the pieces were then shaved smooth and bright with a sharp penknife. By subjecting these pieces to the procedure just described, 0.013 percent of white residue was left from aluminum *A* and 0.014 percent from aluminum sample 44c. The residues from four of these determinations, representing 15.3 g of metal, were ignited and weighed. After treating with hydrofluoric and sulphuric acids, they were again ignited and weighed. The loss in weight was only 0.2 mg, which indicates that but little if any of the silicon in the samples was present as silica. After the treatment with hydrofluoric acid, the residue was fused with sodium carbonate, the cooled melt was dissolved in diluted hydrochloric acid, ammonium hydroxide was added, and the resulting precipitate, which contained no significant amount of titanium and zirconium, was identified as aluminum hydroxide. This precipitate was ignited and weighed, then it was treated with hydrofluoric and sulphuric acids, and again ignited and weighed. The fact that a loss of only 0.1 mg resulted from the treatment with hydrofluoric and sulphuric acids indicates that practically all the very small amount of silicon in this material was volatilized during the treatment with hydrochloric acid gas and hydrogen.

Any oxide that was formed during the melting and pouring of the aluminum could reasonably be expected to remain in the nonvolatile residue because it must have been heated to at least 660° C (the melting point of aluminum). However, it was not at all certain that the film of oxide which forms on the surface of the metal at room temperature would remain in the nonvolatile residue. Accordingly, three portions of a standard solution of aluminum chloride, each equivalent to 0.0095 g of Al_2O_3, were converted to the hydroxide. The first portion was ignited for 1 hour at 600° C, the second was dried for 20 hours at 95° C, and the third was dried at room temperature over concentrated sulphuric acid for 20 hours. These were then separately subjected to the procedure of volatilization just described. No volatilization occurred in any case.

It was realized, however, that the evidence for the nonvolatility of the oxide in hydrochloric acid gas and hydrogen would be more convincing if the determination could be made on a piece of aluminum with a film of oxide of known weight. In an attempt to produce such a film, two bright pieces of aluminum, having a surface area of 10.5 cm^2, were placed in a tube through which a stream of oxygen was passed. No weighable film was formed in 3 days at room temperature. Intermittent heating in oxygen between 50 and 200° C for 24 hours also failed to produce a weighable film. A film of hydrated oxide was finally obtained by placing the pieces of aluminum in a platinum crucible and keeping them partially covered with water at temperatures between 25 and 95° C for 20 days. These pieces of metal were then dried in an oven at 95° C. The increase in weight was 0.0014 g. The weight of the oxide, Al_2O_3, after volatilizing the metal as chloride, was 0.0018 g.

By spreading aluminum hydroxide in a very thin film on the inside surface of a platinum crucible and drying at 95° C for 20 hours, a hydrated oxide corresponding approximately to $Al_2O_3.2H_2O$ was obtained. If it is assumed that the increase in weight of 0.0014 g was caused by the formation of $Al_2O_3.2H_2O$ on the pieces of aluminum, then 0.0008 g of oxygen was combined with aluminum to form the

oxide, Al_2O_3. This corresponds to 0.0017 g of Al_2O_3[21]. A determination of oxide on freshly cut pieces of aluminum, similar to those on which the film of oxide was formed, yielded a residue of 0.0003 g. The weight of oxide that should have been found is, therefore, 0.0017 g + 0.0003 g = 0.0020 g, as compared with 0.0018 g, the weight actually found. If the uncertainty of the composition of the film is taken into account, this must be considered as fairly good evidence that no volatilization of aluminum oxide took place.

Observations indicated that if aluminum is converted to the *anhydrous chloride*, the latter is volatile in a stream of dry hydrochloric acid gas and hydrogen, but that if the chloride is allowed to *hydrate*, it remains in the nonvolatile residue. To confirm this, 0.1000 g of the hydrated chloride, $AlCl_3.6H_2O$, was put in a platinum boat and subjected to a stream of hydrochloric acid gas and hydrogen exactly as was done in the determination of oxide in the metal. All the aluminum chloride remained in the platinum boat. This behavior accounts for the fact that large nonvolatile residues were obtained in the preliminary experimental work when the hydrochloric acid gas and hydrogen were inadequately dried before they came in contact with the metal.

(k) PHOSPHORUS

A 5.0-g portion of metal was dissolved in diluted nitric acid (1+1) to which small portions of hydrochloric acid were added from time to time. The solution was evaporated nearly to dryness on the steam-bath, 50 ml of nitric acid was added, and the solution was again evaporated nearly to dryness. The sirupy residue was dissolved in 100 ml of diluted nitric acid (1+2), the solution was nearly neutralized with ammonium hydroxide, and molybdate reagent was added. The solution was shaken for 10 minutes and allowed to stand for one-half hour. No precipitate appeared. In a solution similarly prepared but to which 0.05 mg of phosphorus was added in the form of a standard solution of phosphoric acid, a definite yellow precipitate appeared at the end of one-half hour. This indicates that if phosphorus is present, the amount is less than 0.001 percent.

IV. PROCEDURES AND RESULTS

1. CHEMICAL REAGENTS AND PLATINUM CRUCIBLES

Hydrochloric acid, sulphuric acid, and ammonium hydroxide were the only reagents used in this part of the work. The acids, bought on the specifications for analytical reagent chemicals recommended by the Committee on Analytical Reagents of the American Chemical Society, were of such good quality that it was not necessary to purify them. None of them yielded a nonvolatile residue exceeding 0.2 mg when 100-ml portions were evaporated and the residue ignited. As less than 30 ml of the combined acids was involved in any determination, and especially since exactly the same quantities were used in blank determinations, these small amounts of impurities were entirely negligible. The ammonium hydroxide was prepared by passing gaseous ammonia into distilled water contained in a Pyrex flask whose inside surface was covered with paraffin. A 100-ml portion of this

[21] When $Al_2O_3.2H_2O$ is formed on the surface of the metal, the addition of oxygen and water causes the increase in weight. Therefore, $3\ O + 2H_2O = 0.0014$ g. The oxygen combined with Al to form $Al_2O_3 = 4/7 \times 0.0014 = 0.0008$ g. And 0.0008 g O $\simeq$ 0.0017 g Al_2O_3.

ammonium hydroxide yielded a residue weighing less than 0.1 mg, even after the solution had stood in the flask for over 9 months.

In work involving prolonged ignitions at high temperatures it is essential that the crucibles do not change weight or that two or more crucibles are available that change weight at a uniform rate. In the determinations reported in this paper one platinum crucible, from a series of four having the same composition, was used as a tare. The crucibles were made of platinum containing 3.5 percent of rhodium and had a capacity of 40 ml. The whole set was heated in a platinum-wound muffle furnace for 5 hours at 1,200 to 1,300° C, cooled, and weighed. Then the crucibles were again heated for 15 to 25 hours at 1,200 to 1,300° C, cooled, and weighed. One crucible, compared with the tare, showed an apparent change in weight of more than 0.1 mg during this latter period of heating and was therefore rejected.

2. CONVERSION OF METALLIC ALUMINUM TO ALUMINUM OXIDE, Al_2O_3, THROUGH THE HYDROXIDE

For the conversion of the metal to the oxide through the hydroxide, a piece of aluminum weighing approximately 2 g was cut out and prepared by the procedure described under III, j, p. 10. It was then carefully weighed and transferred to a 125-ml Pyrex Erlenmeyer flask whose neck was drawn to about one-half its original diameter and three times its original length. After adding 90 ml of diluted hydrochloric acid (1+2), the flask was covered with a Pyrex watch glass and placed on the steambath. These precautions prevented loss by spraying during the very slow solution of the metal, which required 3 or 4 days. For the determination of a "blank", about 4 mg of the same aluminum was carefully weighed and transferred to a similar flask to which the same quantity of acid had been added. From this point the contents of the two flasks were subjected to the same treatments, and the proper correction for the aluminum added to the blank was applied at the end of the determination. The small amount of aluminum was added to the blank to serve as a gatherer of traces of impurities that might otherwise have escaped precipitation.

After the aluminum was dissolved, the solution was transferred to a 250-ml Pyrex beaker and diluted to 150 ml. After adding a few drops of methyl red indicator, ammonium hydroxide was added until the color of the indicator just turned yellow. The beaker was allowed to stand on the steambath for 5 minutes. Then the precipitate was transferred to large ashless filters and washed thoroughly with hot water to remove ammonium chloride which, if not removed, has a tendency to crystallize at the edge of the paper and cause mechanical losses during the drying of the precipitate. The filtrate and washings were slightly acidified with hydrochloric acid; the solution was evaporated to a volume of 40 to 50 ml; and ammonium hydroxide was again added until the color of the indicator just turned yellow. After digesting on the steambath for 15 minutes, this solution was allowed to stand overnight at room temperature, and the small precipitate which separated was removed by filtration and combined with the first precipitate. A dilute solution of ammonium chloride, whose pH was adjusted to about 6.2, was used for washing this last precipitate.

The filtrate was transferred to a clean platinum dish and heated until nearly all ammonium salts were expelled. A few drops of hydrochloric acid and 5 ml of water were added to the residue. The dish and contents were heated on the steambath for a few minutes, and the solution was poured through a small filter. The filtrate, having a volume of about 15 ml, was neutralized with ammonium hydroxide as before and allowed to stand for 24 hours. Although no precipitate was visible, the solution was poured through a small filter which was then added to the precipitates previously obtained.

The filters containing the precipitates were transferred to platinum crucibles which had been tested for constancy of weight, as previously described. In each case the filter paper containing the small amount of precipitate obtained from the aluminum that was added to the blank was placed in the crucible used as a counterpoise. Special care was taken to use in the blank the same number of filter papers of the same size and from the same lot as were used in the regular determination. Tests for uniformity of the ash content of the filter papers were also made. The weights of the ash from three sets of papers, similar to those used to collect the aluminum hydroxide, were found to be identical within the limits of accuracy of weighing. After the precipitates were dried in an oven, the crucibles were partially covered and placed in a cold muffle furnace which was gradually heated to 1,200° C during the course of about 10 hours. The residues were then heated in the covered crucibles at 1,200 to 1,300° C until constant weight was obtained. All final weights remained constant within 0.1 mg during heating for at least 20 hours between 1,200 and 1,300° C, and two of the ignited precipitates were heated for over 50 hours between these two temperatures without showing any change in weight.

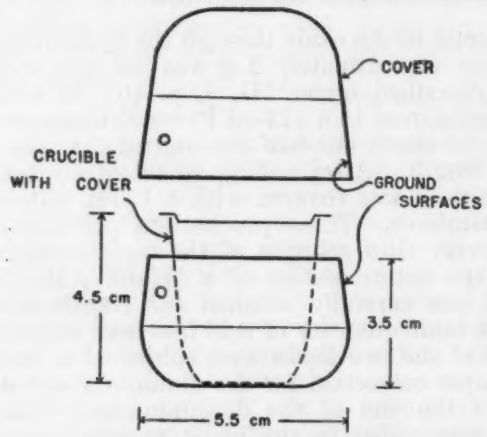

FIGURE 2.—*Glass weighing bottle.*

Since it was found that aluminum oxide is still slightly hygroscopic after these prolonged ignitions, the hot crucibles were taken from the furnace and immediately placed in Pyrex weighing bottles, one of which is illustrated in figure 2. The lower portion of the bottle is only about 3.5 cm high so that the crucible can be set in it with Blair crucible tongs without disturbing the lid of the crucible. The covers were then placed on the bottles so that there was only the slightest meshing between the small holes of the cover and bottle to permit equalization of pressure during cooling. After cooling for 1 hour in a desiccator over concentrated sulphuric acid, the bottles containing the crucibles and aluminum oxide were weighed. In all weighings a similar bottle, containing the platinum crucible with the small quantity of oxide derived from the aluminum added to the blank, was

used as a counterpoise. In calculating the atomic weight, the weight of the sample of aluminum (about 2 g) minus the small amount of metal (about 4 mg) added to the blank was taken as the weight of aluminum metal that was converted to the oxide. Then the difference between the two weights of oxide thus obtained represented the weight of oxide that corresponded to this weight of aluminum, since the blanks on the reagents and glassware were equally operative in both cases and cancelled each other. The determinations were usually made in pairs, and in a few cases as much as 0.1 g of pure aluminum was added to the blank.

All weighings were made with a Ruprecht balance which had a sensitivity of seven scale divisions for 1 mg at a 2-g load and five scale divisions for 1 mg at a 135-g load, the former being the load during the weighing of the metal, and the latter the load during the weighing of the aluminum oxide, including the platinum crucibles and glass weighing bottles. The weight of the metal could easily be reproduced within 0.03 mg on repeated weighings, but reproducibility within 0.1 mg is the best that could be attained in weighing the oxide. It was more convenient to make direct weighings than to weigh by substitution. Because the ratio of the length of the balance arms changed slightly with load, corrections for this effect were made, although these were practically negligible. The weights were carefully calibrated by the Mass Section of the National Bureau of Standards before this work was started and after it was finished, and the proper corrections were made. By weighing with a counterpoise, the use of brass weights in excess of 10 g was avoided. Errors caused by the effect of changes in humidity on the brass weights were therefore negligible. All weights were corrected to the vacuum standard, 2.702 being used as the density of the metal and 4.00 as the density of aluminum oxide,[22] Al_2O_3. Corrections for the very small amounts of impurities in the metal were made by subtracting the weight of the impurities as the elements from the weight of the metal and then subtracting their calculated weight as the oxides from the weight of the ignited oxide.[23] The correction for the small amount of oxide contained in the aluminum (see III, 2, j, p. 10) was made by subtracting its weight both from that of the metal and from that of the ignited oxide.

In three cases it was possible to remove the alumina completely from the crucibles by rubbing gently with the fingers and moist filter paper after the ignitions and weighings were finished. The weights of the crucibles, as compared with the counterpoise, had not changed more than 0.1 mg, and a careful spectrochemical test, capable of easily detecting 0.003 percent of platinum, revealed no platinum in this oxide. The results that were checked in this manner are marked with an asterisk (*) in table 2. It is obvious that such a check was not possible in the series in which the oxide was formed by ignition of the sulphate.

The results obtained by converting the metal to the oxide through the hydroxide are shown in table 2.

[22] Int. Critical Tables 1, 103, 136 (McGraw-Hill Book Co., New York, N. Y., 1926).

[23] For example, aluminum *A* contains 0.006 percent of silicon which in a 2-g sample is equivalent to 0.12 mg of Si and 0.26 mg of SiO_2. Thus, in the case of silicon, 0.12 mg was subtracted from the weight of the metal and 0.26 mg from the weight of the oxide.

TABLE 2.—*Results obtained for the atomic weight of aluminum by converting the metal to the oxide through the hydroxide*

Number	Weight of aluminum	Weight of Al_2O_3	Calculated atomic weight
	g	g	
1[a]	2.00100	3.78105	26.979
2[b]	1.89511	3.58079	26.982
3[b]	1.83837	3.47351	26.983
4[a]	1.88787	3.56752	[c] 26.975*
5[a]	1.90155	3.59348	26.974*
6[b]	2.33772	4.41805	26.970
7[b]	1.99419	3.76859	26.973*
Average			26.977 ±0.004

[a] Aluminum sample no. 44c.
[b] Aluminum *A*.
[c] The values marked with an asterisk (*) were checked by weighing the platinum crucibles after the prolonged ignitions.

3. CONVERSION OF METALLIC ALUMINUM TO ALUMINUM OXIDE, Al_2O_3, THROUGH THE SULPHATE

The metal (about 2 g) was dissolved as described in the previous procedure, and the hydrochloric acid was removed by adding 7 to 10 ml of sulphuric acid and evaporating until fumes of the latter appeared. The residue was cooled, 15 to 20 ml of water was added, and the resulting solution was transferred to a platinum crucible that had been tested for constancy of weight as compared with a similar crucible as a counterpoise in the manner previously described. Exactly the same quantities of acids were carried along as a blank, and the residue resulting from the blank was ignited in the platinum crucible used as a counterpoise. The small flasks in which the metal was dissolved were repeatedly washed with water and the rinsings added to the contents of the crucibles. These additions were made possible by evaporating part of the water from the crucibles between rinsings.

TABLE 3.—*Results obtained for the atomic weight of aluminum by converting the metal to the oxide through the sulphate*

Number	Weight of aluminum	Weight of Al_2O_3	Calculated atomic weight
	g	g	
1[a]	1.88650	3.56504	26.973
2[b]	2.00812	3.79482	26.974
3[b]	1.63804	3.09555	26.973
4[b]	2.65087	5.00956	26.973
5[b]	2.64428	4.99696	26.975
6[b]	2.04031	3.85588	26.971
7[b]	1.72393	3.25736	[c] (26.982)
Average			26.973 ±0.001

[a] Aluminum sample 44c.
[b] Aluminum *A*.
[c] The value in parentheses was omitted in averaging the results because its deviation from the mean of the other results is greater than 4 times the average deviation.

When it was certain that all the aluminum sulphate had been transferred, as much as possible of the water was evaporated on the steambath. Then the crucibles were partially covered and transferred to radiators,[24] and heat was *very* gradually applied until the excess

[24] See W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, p. 22 (J. Wiley & Sons, N.Y. 1929 ed.).

sulphuric acid was volatilized. The crucibles and contents were next placed in a muffle furnace, which was gradually heated until sulphur trioxide began to be evolved. This occurred at about 800° C, and during this evolution the temperature was regulated to remain practically constant in order to avoid too rapid a decomposition of the sulphate, which might result in mechanical losses. After a noticeable evolution of sulphur trioxide had ceased, the crucibles were covered, transferred to a platinum-wound furnace, and the temperature was raised to 1,200 to 1,300° C. The ignition was then continued until constant weight was obtained. The weighings were made as in the previous procedure. The results obtained are shown in table 3.

V. DISCUSSION OF RESULTS

Tests indicate that the recorded weights of the metal are accurate within 0.03 mg and the weights of the oxide within 0.1 mg. If errors of this magnitude were made in weighing, and if they were in the same direction in weighing the metal as in weighing the oxide, they were practically without effect; but even if they were in opposite directions, they would cause an error of only 0.0024 in the atomic weight, assuming that 2 g of metal was converted to the oxide.

The result of the hydroxide series is 26.977 ±0.004; that of the sulphate series is 26.973 ±0.001; and their average, weighted inversely[25] as the indicated uncertainties, is 26.974 ±0.002. The indicated uncertainties are in all cases three times the probable error.

Krepelka,[26] from the ratio, $AlCl_3$:3Ag, obtained 26.972 ±0.001 by using 107.880 and 35.458 for the atomic weights, respectively, of silver and chlorine. If the present atomic weight of chlorine (35.457) is used, this value becomes 26.975, and if the uncertainty is expressed as three times the probable error, Krepelka's value becomes 26.975 ±0.003. Later, Krepelka and Nikolic[27] from the ratio, $AlCl_3$:3Ag, obtained 26.974 ±0.001 by using 107.880 and 35.457 for the atomic weights, respectively of silver and chlorine. From the ratio $AlCl_3$:3AgCl, they obtained 26.972. If the average of these two values is taken and an uncertainty of ±0.003 is assigned to it, their value becomes 26.973 ±0.003.

According to Krepelka's work, the atomic weight of aluminum lies between 26.972 and 26.978, according to Krepelka and Nikolic's work it lies between 26.970 and 26.976, and according to the present work it lies between 26.972 and 26.976. Since the values between 26.972 and 26.976 are common to the three, and since three different ratios were employed in obtaining them, the atomic weight of aluminum might properly be given in the International Atomic Weights to three decimal places somewhere between the limits 26.972 and 26.976.

Aston's work[28] with the mass-spectograph indicates that aluminum has no isotopes and that the mass of Al^{27} is 26.9909[29] (O^{16}=16.0000). This provisional value, when corrected to the chemist's scale by using the conversion factor 1.00020 to take into account the heavier isotopes of oxygen, becomes 26.9855. This leaves a discrepancy of approximately 0.01 between the chemically determined atomic weight and

[25] Usually such values are weighted inversely as the square of their probable errors, but since three of the results given in the hydroxide series were checked by weighing the crucibles after the ignitions, it seems unreasonable to give the average of the hydroxide series only 1/16 the weight given to the sulphate series.
[26] H. Krepelka, J. Am. Chem. Soc. **46**, 1343 (1924).
[27] H. Krepelka and N. Nikolic, Chem. Listy **19**, 158 (1925) and Chem. Abstracts **19**, 3179 (1925).
[28] F. W. Aston, Mass-spectra and Isotopes, p. 125 (Edward Arnold and Co., London, 1933).
[29] Nature **137**, 613 (1936). The value given is stated to be only provisional.

that obtained by the use of the mass-spectrograph. If it is assumed that the latter is correct, an error would have to exist in the present chemical determination which could be explained only by assuming (1) that the aluminum metal contained impurities other than those detected chemically or spectrochemically, or (2) that an average positive error of 0.7 mg was made in determining the amount of aluminum oxide. Impurities that could possibly cause the weights of oxide to be high, and the atomic weight to be low, are boron, silicon, beryllium, lithium, sodium, potassium, magnesium, calcium, and strontium. The first three have higher factors than aluminum for conversion of the element to the oxide, and the others might be retained as sulphates when the aluminum metal is converted to the oxide through the sulphate. The last six can be excluded because (1) chemical and spectrochemical tests indicated the absence of significant amounts of these, (2) no sulphate could be detected in the oxide that was formed by converting the metal to the oxide through the sulphate, and (3) the values obtained by igniting the sulphate are in such excellent agreement with the best values (marked * in table 2) obtained by igniting the hydroxide after the aluminum was precipitated by ammonium hydroxide. In this latter procedure most of all six elements last mentioned would have been eliminated.

Boron in the original metal would have caused low weights of oxide because it is readily lost as boron hydride or by volatilization with steam as boric acid during solution of the metal in acid.[30] Furthermore, a special spectrochemical test whose sensitivity is not definitely known but which was capable of detecting 0.001 percent of boron in silver metal failed to reveal any boron in the aluminum. The care with which silicon was determined and the special test that was made for beryllium show clearly that no significant error could have been introduced by silicon and beryllium. This excludes all obvious possibilities of accounting for a discrepancy of 0.01 in the atomic weight by assuming the presence of impurities in the metal. Spectrochemical tests showed that the alumina obtained in both procedures contained less than 0.001 percent of boric oxide. This, together with the tests on the aluminum oxide previously described, indicates that an average positive error of 0.7 mg in determining the amount of oxide is altogether unlikely.

If our value for the atomic weight, 26.974, is converted to the physicist's scale ($O^{16}=16.0000$), 26.9794 is obtained, and the packing fraction calculated from this is -7.6 as compared with Aston's value of -3.4. If these values for packing fraction are plotted as ordinates against mass numbers as abscissas, our value falls considerably below the curve obtained for the lighter elements, whereas Aston's value falls more nearly on the curve.[31] Of course, any errors that may exist in the values appear magnified by plotting a curve in this manner, and no definite conclusions can be drawn until more work is done with the mass-spectrograph and until a reasonable uncertainty is assigned to the value thus obtained.

The value for the atomic weight of aluminum based on the conversion of the metal to the oxide is 26.974 $\pm$0.002.

WASHINGTON, October 13, 1936.

[30] H. V. Churchill and R. W. Bridges, Chemical Analysis of Aluminum, Aluminum Research Laboratories, New Kensington, Pa. (1935).

[31] See Mass-spectra and Isotopes, p. 168 (1933).

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP958

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

METHODS OF DETERMINING GLOSS[1]

By Richard S. Hunter

ABSTRACT

Glossiness is evidenced by almost every object and is to be attributed to specular reflection. Specular reflection occurs at the surfaces of reflecting objects; and, because of the diversities of minute surface structure, many kinds of glossy appearance result. An attempt to classify these glossy appearances has led to the description of six different kinds of gloss: (1) specular gloss, identified by shininess; (2) sheen, identified by surface shininess at grazing angles; (3) contrast gloss, identified by contrasts between specularly reflecting areas of surfaces and other areas; (4) absence-of-bloom gloss, identified by the absence of reflection haze or smear adjacent to reflected high lights; (5) distinctness-of-reflected-image gloss, identified by the distinctness of images reflected in surfaces; and (6) absence-of-surface-texture gloss, identified by the lack of surface texture and surface blemishes.

In describing the appearances of objects, one commonly distinguishes between the effects due to two types of reflection; glossiness, on the one hand, may be correlated with specular, or surface reflectance; the degree of lightness or darkness may, on the other hand, be correlated with diffuse reflectance usually occuring within the pigmented and scattering media beneath these surfaces. Specular reflection is evidenced by light preponderantly reflected in the direction of mirror reflection, whereas diffuse reflection is evidenced by light scattered in all directions by the reflecting object. Unfortunately for the purposes of gloss and reflectance measurement, the effects of specular reflection and diffuse reflection cannot be completely separated. The gloss of a surface cannot, in the general case, be defined in any simple way that permits quantitative measurement.

Data which describe the directional distribution of light reflected by surfaces illuminated under specified conditions furnish the fundamental physical basis for describing gloss. However, such distribution data are cumbersome and involved and include the effects of both diffuse and specular reflection. It is because these goniophotometric (reflection distribution) data are unwieldy that, in the past, devices for measuring gloss have been developed by simple empirical means. By trial and error, methods have been found to measure the gloss of particular types of materials exhibiting particular types of gloss.

The article suggests that the designer of a prospective gloss meter should determine from goniophotometric data taken on representative samples what differences in apparent reflectance are most characteristic of the differences in glossiness observed visually. That is, gloss-meter design will have considerably less of the trial-and-error element when goniophotometric data are used to indicate the most pertinent reflectance measurements to make for various purposes.

Also included are descriptions of typical gloss instruments, descriptions of measurements they make, and a bibliography on gloss. Differences between the various types of gloss are analyzed in some detail.

[1] This paper was presented before the Thirty-Ninth Annual Meeting of the American Society for Testing Materials, Atlantic City, July 3, 1936. Preliminary papers on the same subject were presented before the Optical Society of America, in Washington, October 20, 1934, and in Philadelphia, October 25, 1935. (See reference [19] in bibliography.)

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I. INTRODUCTION

Gloss is possessed by most materials encountered in everyday life, and its occurrence is so common that persons seldom stop to give it particular notice. People are, nevertheless, responsive to the general appearance of objects and nearly everyone is able to form opinions as to the beauty, attractiveness, or striking appearance of things they see. Gloss is one of the major factors in appearance, and a number of methods for determining it have been developed. The purpose of these methods is usually to enable the producers and vendors of articles in commerce to rate them according to glossiness.

1. DEFINITIONS

It should be noted that the term "gloss" is used in this paper in a general sense to include all properties of surfaces responsible for effects such as "shininess", "sheen", "lustre", etc. Following Jones [24],[1] *gloss* and *glossiness* are here defined so that the actual physical properties of surfaces responsible for their glossy appearance may be distinguished from the appearance itself. That is, the *gloss* of a surface is considered to be a property of the surface; *glossiness*, the appearance that results because the surface possesses that property.

1. The *gloss* of a surface is its power to reflect light specularly. Since, unfortunately, specular reflectance is a quality which may not be separated by any objective measurement from diffuse reflectance in any but special cases, this definition of gloss does not, in general, describe a quantity that can be unambiguously measured until, in addition, the conditions of measurement are precisely stated. (See section V, p. 28.)

2. The *glossiness* of a surface is the appearance which results from its power to reflect light specularly. For any given surface, glossiness may vary with conditions of illumination and directions of view, but gloss is considered to be an inherent quality.

3. *Specular reflection* is that kind of reflection which causes surfaces to exhibit high lights and to appear somewhat like a mirror. This definition of specular reflection describes the process in terms of the appearance it produces and consequently does not explain the physical

[1] Numbers in brackets refer to the corresponding reference number in the bibliography at the end of this paper.

cause of gloss. Specular reflection is commonly contrasted with diffuse reflection, which is likewise defined in terms of the appearance it produces.

4. *Diffuse reflection* is that kind of reflection which causes a surface to possess lightness or darkness of some degree which may be represented on the scale of grays running from white to black. Specular reflection and diffuse reflection are constantly used in technical descriptions of the appearance of objects. Unfortunately there is no general way in which effects of these two processes may be accurately separated. It is impossible to measure specular reflectance and diffuse reflectance as separate entities in any but an approximate way. Consequently, the separate effects of the two processes cannot be rigorously specified; and the two processes are, for this reason, defined in the present paper in terms of the appearance each produces, even though it is customary to think of them as physically separate processes dependent upon the structure and composition of the object. Specular and diffuse reflection are discussed further in section IV, p. 26.

5. *Apparent luminous reflectance*, hereinafter termed *apparent reflectance*, is defined as the luminous reflectance a perfectly diffusing surface must have in order to yield the same brightness as the unknown surface under the same conditions of illuminating and viewing [35]. That is, any surface observed in any manner and illuminated by any combination of illuminants is compared to the theoretical, perfectly reflecting, perfectly diffusing surface observed and illuminated under exactly the same conditions. (See fig. 2 and section III.) In practice, of course, the theoretical, perfectly reflecting, perfectly diffusing surface is not obtainable, but material standards of known apparent reflectances may be obtained in several ways. For many cases, relative apparent reflectances are all that are needed and standards of known apparent reflectances are not required.

The plan of the present paper is to describe first the six different types of gloss in terms of the appearances they produce. Following this is a discussion of the directional distribution of light reflected by surfaces and the various measures thereof. With information thus at hand on the appearance characteristics resulting from the different types of gloss and on the basic method of reflectometry which is inseparable from the discussion of gloss, it becomes possible to develop relationships between these two phases of the subject.

II. SIX TYPES OF GLOSS

The necessity for a classification of gloss types arises when one attempts to grade materials for gloss, or to describe their differences in appearance. With two materials of the same general appearance, it is possible to say that one or the other has the higher gloss, or that the two appear about the same. For two materials of different appearance, however, it often cannot be stated which has the higher gloss. They may not show a common type of glossiness by which they may be graded.

From a study of the appearance by which the gloss of surfaces is commonly graded and from a study of the different existing gloss-measuring instruments and the properties they measure, a classification of gloss into six types has been devised. A classification was first made by the author in the fall of 1935 when, however, only five types were identified [18]. Table 1, which gives the classification, is

TABLE 1.—*Classification of the six types of gloss*

Type of gloss	Appearance characteristics produced	Most often used to describe appearance of—	Gloss range	References in bibliography
Specular gloss (formerly objective gloss).	Brilliance of specularly reflected light, shininess.	Paints, surfaces of moderate gloss, dark and chromatic objects.	Medium gloss.	[3, 5, 14, 16, 17, 23, 31, 32, 39, 43, 44, 47, 52, 54.]
Sheen	Shininess at grazing angles.	Flat paints, papers, and materials of low gloss.	Low gloss	[37, 44.]
Contrast gloss (formerly subjective gloss).	Contrast between specularly reflecting areas and other areas.	Papers, mat and semimat finishes, white and light-colored materials.	Low gloss	[7, 8, 9, 11, 12, 15, 22, 24, 25, 26, 27, 28, 29, 33, 34, 44 45, 46, 48, 49.]
Absence-of-bloom gloss.	Absence of smear or excess semi-specular reflection adjacent to reflected high lights and images.	Surfaces in which reflected images and high lights may be seen.	High gloss	[21, 26.]
Distinctness-of-reflected-image gloss.	The distinctness and sharpness of reflected images.	Finishes, enamels, lacquers, and all smooth image-reflecting surfaces.	High gloss	[10, 18, 21, 43, 51, 53.]
Absence-of-surface-texture gloss.	Surface evenness, absence of texture, indicated by difficulty of recognizing presence of surface.	Glossy materials, finishes, and coatings.	Medium to high gloss	[17.

a modification of the previous table and lists: (a) the six types of gloss; (b) the appearance characteristics of each; (c) materials with which each type of gloss is most often identified; (d) the position in the general gloss range in which surfaces possessing each of the types of gloss are most often found; and (e) references to instruments which measure each type of gloss. Figure 1, reproduced from this article [18] serves to illustrate some of these types and shows photographs of gloss-comparator images reflected in four pairs of surfaces. The first two surfaces differ essentially in specular gloss, the second two in contrast gloss, the third two in bloom, and the fourth two in surface texture. Variations in distinctness-of-reflected-image gloss are also seen; for instance, the first two samples reflect images quite accurately, but the second two do not. Sheen, which was only recently added to the list, is not illustrated. Further details regarding these types of gloss, their significance and their measurement, are given in the later sections of this paper and in other papers [18, 19, 20].

This scheme of identifying gloss types is based upon observation and upon methods of classification and grading gloss that are already in existence. It is not intended to be the final and complete method for describing gloss and glossiness. There seem to be several types of glossiness that are not adequately explained by this analysis; for instance, some of the appearances that are associated with degree of polish are particularly hard to describe in the terms given in table 1. It is possible, however, that these effects may be treated as combinations of several of the types of gloss already identified. Many more data are needed on the correlation of differences in glossiness identified by observers and the results of instrumental measures of gloss. Viewed under different conditions, surfaces apparently present more than six different types of glossiness.

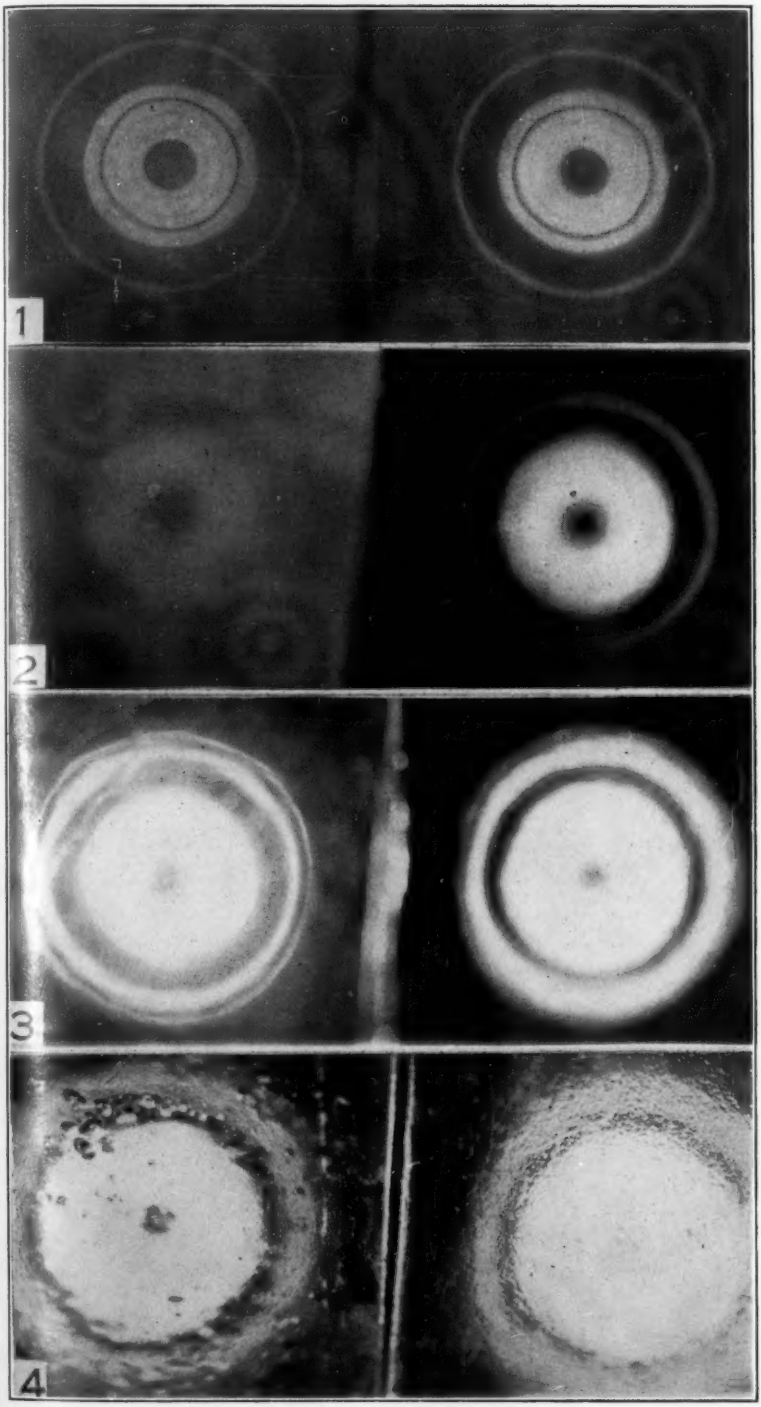

FIGURE 1.—*Images photographed with gloss comparator [18] showing types of gloss.*

1. The right image is brighter than the left image and depicts higher specular gloss. 2. The right image is from a black surface, the left image from a white surface. The black surface shows higher contrast gloss. 3. Although the left image is sharper, it shows reflection smear, or bloom. 4. Camera focussed on surfaces to record texture. Left: Pimpled; right: Orange peel.

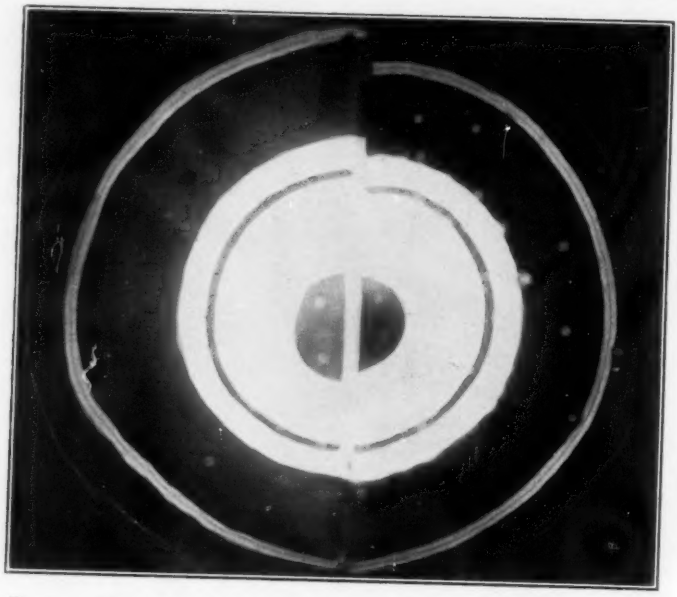

FIGURE 11.—*Gloss lamp target [21] reflected in pair of surfaces.*

The specimen on the left shows the reflection haze due to its bloom in the dark area of the image adjacent to the bright center circle. See text, page 35.

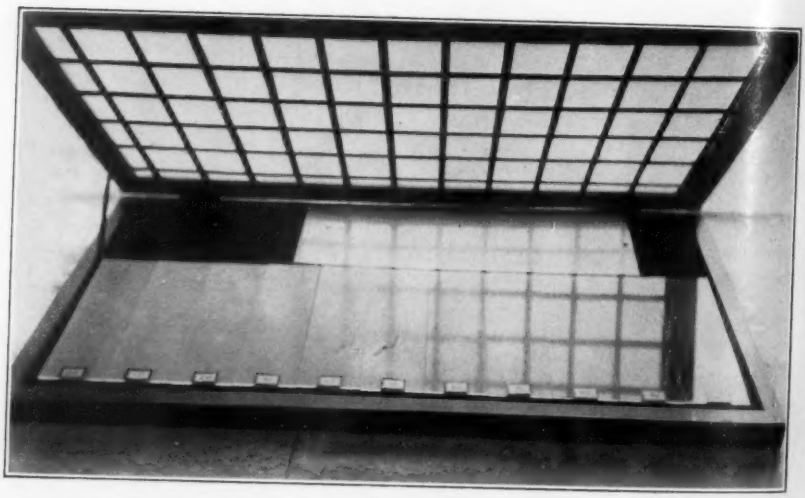

FIGURE 12.—*Detroit Paint Production Club method of rating distinctness-of-reflected-image gloss [10].*

The series of standard lacquers of varying distinctness-of-reflected-image gloss are arranged in a row and compared to any test sample. See text, page 35.

The need for simplicity in the treatment of the subject must be compromised with the need for an analysis of the problem complete enough to include within its scope methods of answering most of the questions that will arise. As an indication of the adequacy of table 1, it may be noted that it served to place, according to type of gloss measured, every one of the thirty-seven methods of measuring and analyzing gloss listed in the bibliography. On the other hand, some of the effects described in the papers dealing with the phenomenological and psychological phases of the subject were difficult to represent in terms of the six-gloss-type classification.

Smooth metal surfaces exhibiting metallic glossiness are distinguished by the fact that a major portion of the incident light is reflected specularly; whereas but 3 to 8 percent of the incident light is reflected specularly from nonmetallic surfaces at the nongrazing angles. Thus a major portion of the light incident upon a nonmetallic surface may be reflected diffusely whereas metallic surfaces are commonly characterized by a relative lack of diffuse reflectance. In spite of these differences, it is believed that, inasmuch as both metallic and nonmetallic surfaces exhibit specular reflectance, the above classification designed to describe nonmetallic surfaces may also be used to describe metallic surfaces. At present, however, no data are at hand to show the applicability of the six-type classification to descriptions of metallic appearance.

III. DIRECTIONAL DISTRIBUTION OF REFLECTED LIGHT

In this section the reflectance characteristics of surfaces responsible for glossy appearance are treated. Data describing the intensity distribution of incident and reflected light as a function of angle form the physical bases for descriptions of gloss. Such data are commonly presented as curves or numerical values giving, for specified angular distributions of illumination, values of apparent reflectance for different directions of reflection.

In figure 2, two experimentally obtained reflection-distribution curves are given together with a theoretical curve for comparison. In this diagram, light from a single direction is represented by *I* and is incident upon the reflecting surface, *O*, at 45°. *S* indicates the direction of reflection of this light for the case in which the reflecting surface is optically smooth and mirror-like. The curve *D* gives the apparent reflectance for the theoretical, perfectly reflecting, perfectly diffusing surface which possesses, by definition, an apparent reflectance of unity in all directions. It will be recalled that apparent reflectance is defined as the reflectance a perfectly diffusing surface would have to have in order to yield the same brightness as the unknown surface under the given conditions of illuminating and viewing. Compared to the perfectly diffusing surface, surfaces commonly reflect a disproportionately large amount of light in the general direction of mirror reflection because of gloss; consequently their apparent reflectance may rise to well above unity in that direction.

Curve *M* gives the apparent reflectance for a nearly mat sample of mimeograph paper; and *P* the apparent reflectance for a vitreous, porcelain-enamelled plate. As would be expected, the vitreous porcelain concentrates the reflected light about the direction of mirror reflection, rising to a measured apparent reflectance of 25.0 at 45°. In the case of the mimeograph paper, it can be seen that the apparent

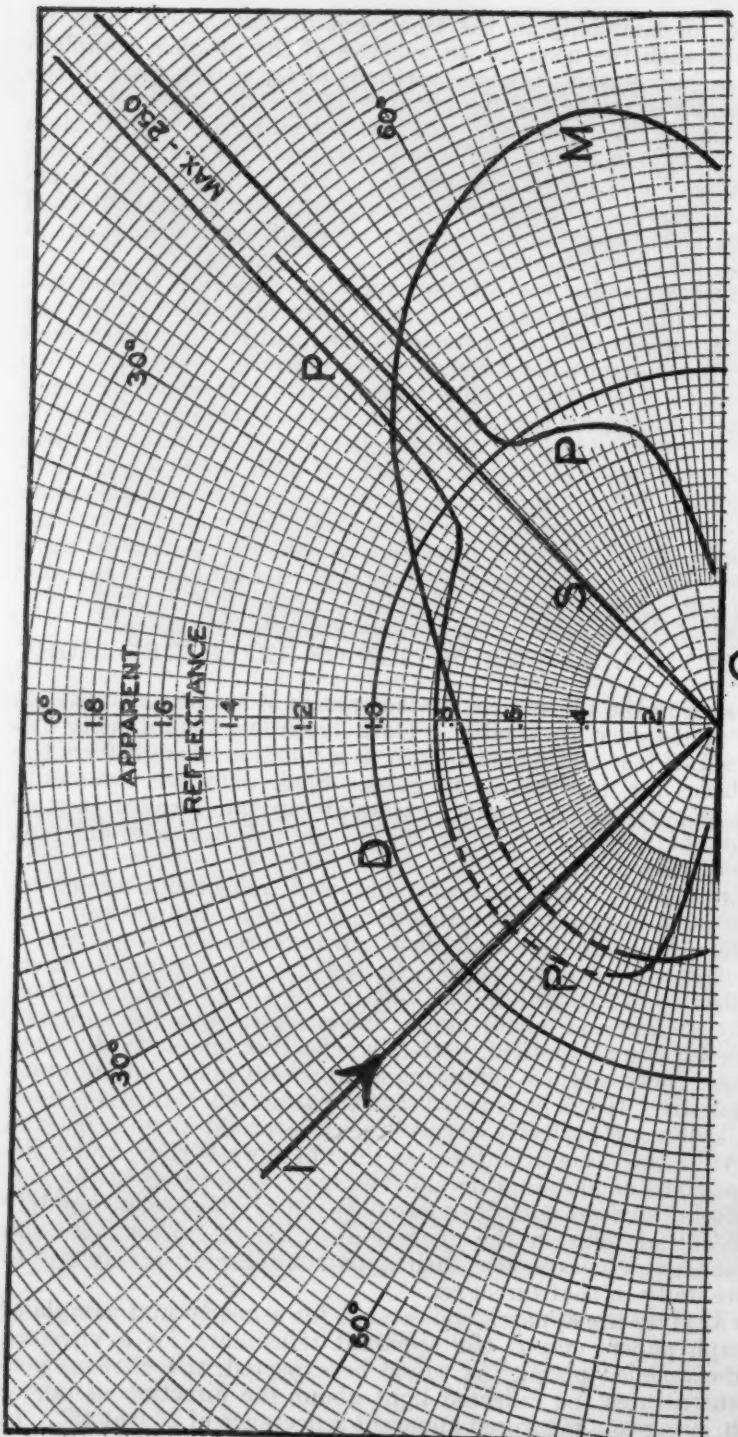

FIGURE 2.—*Reflection distribution curves for porcelain-enamelled plate, P, and sheet of mimeograph paper, M.*

Direction of incident illumination, *I*; direction of mirror reflection, *S*; reflecting surface, *O*; and reflection distribution for ideal, completely reflecting, perfectly-diffusing surface, *D*, also indicated.

reflectance is higher opposite the incident illumination but that there is no concentration of apparent reflectance in the direction of mirror reflection. In fact, it is interesting to note that the highest apparent reflectance appears in a direction further from the normal than mirror reflection. This type of curve is characteristic of many types of nearly mat surfaces.

Because it is known [3] that a freshly prepared magnesium oxide surface illuminated at 45° and viewed normally possesses an apparent reflectance of 1.00, secondary standards of reflectance obtained by comparisons with magnesium oxide are satisfactory standards of apparent reflectance for these conditions. If the apparent reflectance of a given surface is known for one direction of illumination and view together with its relative brightnesses for other directions of view, its apparent reflectances for these other directions may be derived because the brightness of the perfectly diffusing surface does not vary with direction of view.

The complete specification of a surface's ability to direct reflected light is so complex that it is virtually never determined. Light may be reflected by a surface in all directions; furthermore, with an infinite number of possible incident illuminations, each of which may result in a different distribution of light, the complete reflection-distribution specification for any surface is made up of a "quadruple infinity" of apparent reflectances. Instead of complete goniophotometric analyses, partial analyses such as shown by the curves presented in figure 2 are usually adopted. For example, only those values of apparent reflectance in the plane of the 45° incident beam and the normal to the surface are given in figure 2. In using single curves such as these, it must be realized that they do not present in any case the complete physical basis of glossiness and that there may often be reflectance effects of importance to the investigator not indicated by the data given. Thus, for example, figure 2, as it is given, does not show sheen because the illumination is not at grazing incidence.

Jones [24] was the first to emphasize the importance of goniophotometric measurements in gloss work. McNicholas [35] has treated the theoretical side of the subject and, in addition, published many valuable experimental data.

In discussing reflection distribution above, it was assumed that exact values of apparent reflectance for exact unidirectional illuminations and directions of view could be obtained. Actually, it is impossible to obtain curves for true unidirectional illumination and true unidirectional viewing because every source and every receptor used in a reflectance measuring instrument possesses finite size. It is doubtful whether there exists any goniophotometer possessing sufficiently small illuminating and viewing apertures to deal successfully with all gloss problems.

The eye is able to resolve images separated by one minute of visual arc. To equal the eye in distinguishing differences between surfaces of high gloss the goniophotometer should likewise be capable of revealing these effects in terms of brightness. Up to the present time it is believed that no goniophotometer has been produced which possesses this power of resolution. To build such an instrument it will be necessary to have the source and receptor of narrow aperture. For each determination, the light which reaches the reflecting surface from

[3] Preston, J. S., *The reflection factor of magnesium oxide*, Trans. Opt. Soc. London **31**, 15 (1929-30).

the source must follow a path in which all rays are parallel to within one minute of arc, and that reaching the receptor from the reflecting surface must satisfy the same conditions, so that, within this tolerance, light of one, and only one, direction of incidence and reflection is accepted for measurement. Only with such an instrument will it be possible to obtain sufficiently accurate reflection-distribution curves to differentiate all surfaces of high gloss.

Most of the goniophotometers now in use accept, for measurement in one setting, light reflected by the test surface at angles comprising several degrees. Therefore the distribution curves obtained with such instruments are less selective with respect to angle of reflection than are the ideal curves for unidirectional illumination and measurement. That is, each apparent-reflectance value obtained with an instrument of appreciable angular aperture represents the average of apparent reflectances for all the directions included in the measurement. Figure 3 is a diagram of the modification of McNicholas'

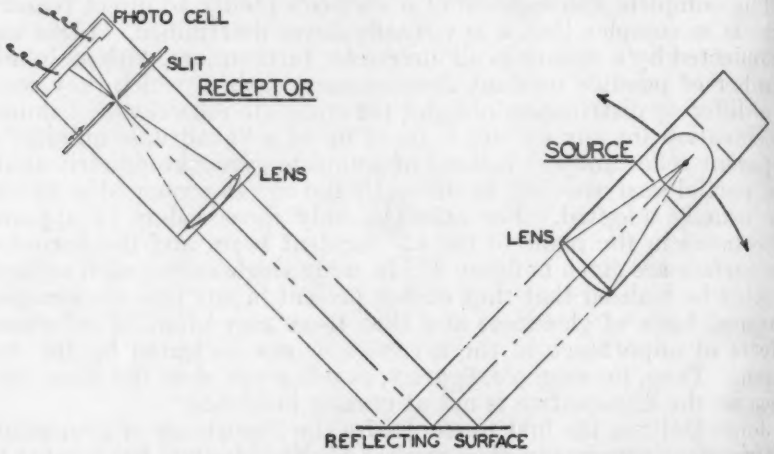

FIGURE 3.—*Photoelectric modification of McNicholas' goniophotometer with narrow source and receptor apertures [36].*

The receptor is fixed in position; the source and reflecting surface may be rotated about the center of the reflecting surface, either separately or together.

goniophotometer [36] constructed at the National Bureau of Standards. This modification has been designed to give high angular resolving power for reflection-distribution measurements. A single coil of a monoplane-filament lamp provides a source of narrow aperture. In front of the photocell receptor is an adjustable slit which can be made as narrow as desired, the only requirement being that sufficient light pass through it to give a current from the photocell that will register satisfactorily. This new apparatus was used to obtain the curves of figure 2. It will resolve about one-half of one degree. The source and sample may be rotated about the axis of the sample position, but the receptor position is fixed.

IV. SPECULAR AND DIFFUSE REFLECTION

In the previous sections gloss types have been classified according to appearance, and the fundamental reflectance method necessary for basic gloss specification has been described. The remainder of the

paper will be devoted to relationships between these two phases of the subject. It was pointed out in the introduction that the concepts of specular and diffuse reflection are widely used in descriptions of the appearance of opaque objects. It has, in fact, been customary to say that specular reflection is responsible for gloss, although in table 1 above it may be seen that absence of diffuse reflection increases gloss of at least one type (contrast gloss).

In order to form a picture of the mechanism of reflection, one should consider the minute reflecting areas of individual particles as well as the larger visible areas of objects. Reflection occurs whenever light encounters a boundary between two media differing in refractive index. Specular reflection is ordinarily "first-surface" reflection taking place at the initial contact of the incident light with the reflecting object—as from enamelled tile. Diffuse reflection is, in most cases, principally a combination of reflection, refraction, and Rayleigh scattering taking place within the body of the reflecting object by the pigment particles and other particles having refractive indices differing from the refractive index of the surrounding medium. Only when the surface of an object is optically smooth is it possible to separate quantitatively the specular reflectance from the diffuse, the former in this instance being confined entirely to the direction of mirror reflection. The porcelain plate, represented by curve *P*, figure 2, is quite smooth. From its reflection-distribution curve, it may be seen that it would be possible to divide the observed reflectance satisfactorily into two components: one, diffuse reflectance, nearly constant in all directions; and the second, specular reflectance, which is the excess in the direction of mirror reflection.

For objects whose surfaces are not optically smooth—and the majority fall in this class—it is not possible to separate the observed reflectance into its components so easily. That is, it is not possible to decide, even approximately, what portion of the reflectance is diffuse and what portion is specular. The mimeograph paper, represented by curve *M*, figure 2, presents a characteristic reflection-distribution in which the usual transition from high reflectance in the approximate direction of mirror reflection to lower reflectance in other directions is wholly wanting—giving no indication of a separation into diffuse and specular components. Typical of materials which possess surfaces that are not optically smooth are semimat, painted finishes whereon protruding pigment particles or voids left after the evaporation of minute pools of volatile liquid break the smoothness of the surface; also sheets of paper in which there are voids between the individual fiber, pigment, and resin particles composing the sheet. Materials such as these frequently present a glossy appearance probably ascribable to a tendency for the individual surface units to follow the surface shape of the object.

Each specimen has its own reflection distribution, and only where the surface as a whole is optically smooth is it possible to separate the diffuse reflectance from the specular reflectance. For materials that differ as much in their power to direct reflected light as the white porcelain and white mimeograph paper of figure 2, the question of whether one or the other is lighter is obviously a question of how they are illuminated and viewed.

V. WHAT GLOSS METERS MEASURE

Most instruments designed to measure gloss actually determine some arbitrarily chosen type of apparent reflectance which has been found by experience to correlate closely with the particular type of gloss being studied. That is, most gloss meters have been designed empirically because few of their designers have had the opportunity to obtain goniophotometric data pertinent to the types of material whose gloss is to be measured.

It is advantageous for the designer of a gloss meter to determine from goniophotometric data on representative samples what particular apparent reflectance, or function of apparent reflectances, correlates best with glossiness, and then construct an instrument to measure this particular function. It is the object of research now being carried forward at the National Bureau of Standards to develop high-precision goniophotometric apparatus to study various gloss problems, to determine to what extent existing gloss-measuring apparatus is applicable to each problem, and to devise new apparatus if existing devices are found inadequate. Only Jones [24] is known to have made goniophotometric measurements on his materials before developing a gloss meter to measure them. The primary requirement for a gloss meter is that it give results which correlate satisfactorily with the gloss ratings on these same specimens assigned by visual inspection. In addition, the instrument should be reproducible from the description, so that the ratings obtained will not depend upon any particular instrument. Other desirable features are portability, inexpensiveness, ruggedness, and simplicity.

Information on three matters is needed in the description of a gloss-determining method: (1) direction and aperture of both incidence and view; (2) spectral composition of the light; and (3) polarization of the light. In describing any method of measuring gloss, the indication of (1) is most significant.

1. DIRECTION AND APERTURE OF INCIDENCE AND VIEW

For a complete description of a reflectance measurement, it is necessary to give the angles of incidence and reflection of all rays of light leaving the source and reaching the receptor by way of the test surface. That is, all those portions of the reflection distribution which enter the measurement must be given. Since every source of light and every receptor must possess finite size, illumination of the sample in any instrument comes not from a single point but from the integral parts of the source. Similarly, light leaving any one point of the surface of the sample may take any one of several directions and be incident upon various parts of the receptor. The elements that determine the possible combinations of angles of incidence and reflection by which light may travel from the source to the receptor are (1) the central directions of incidence and viewing, (2) the solid angular apertures of source and receptor, and (3) the area of the surface tested. Thus to describe completely the reflectance indication of a given gloss meter, it is practically necessary to have a drawing to scale of its complete optical system.

For an approximate angular specification of a gloss measurement, the factors of first importance are the angles which the axial rays of the incident and viewing beams make with the normal to the test

surface. This information is available for practically all gloss meters. Thus, with Jones' gloss meter [24], figure 8, two beams reflected at 0° and minus 45° are compared, the surface being illuminated at 45°. Pfund's instrument [44], figure 5, always makes the angle of view equal to the angle of incidence of the illumination. The Ingersoll glarimeter [22], figure 9, measures the polarization of light reflected at minus 57.5°, with illumination incident at 57.5°.

In addition to the axial directions of illumination and view, data on the angular aperture of the light within the beams are important for the description of a gloss meter. This factor is of major importance in any measurement involving specular reflection, because, as can be seen from the reflection distribution curves above, the angular spread of specular reflectance varies markedly with type of glossy surface. To simplify the description of this factor so that all possible angles of incidence and view do not have to be stated, it is usually sufficient to give the maximum deviation, from the angle of mirror reflection, of any part of the beam accepted for measurement as specular reflection. To arrive at a figure which is fairly indicative of this maximum angular deviation from mirror reflection, one-half the sum of the angular apertures of source and receptor with regard to the reflecting surface may be taken for any instrument. In the case of the Ingersoll glarimeter a cone of light 13° in diameter is incident upon the glossy surface. (See fig. 9.) With the solid angular aperture of the viewing element, an artificial pupil, negligible when compared to the 13° of the source, the maximum angular deviation from the direction of mirror reflection of light accepted for measurement is 6.5°.

2. SPECTRAL COMPOSITION OF THE LIGHT

Spectral specifications include descriptions of the following three factors: (1) spectral distribution of energy from the source; (2) spectral transmissions of any filters in the system, and (3) spectral sensitivity of the viewing element. Almost without exception the instruments now being used to measure gloss employ an incandescent light source but do not use spectral filters [4] to alter the color of this source. Since the majority of instruments are visual, the usual viewing element is a human eye, and this possesses a spectral response similar to the adopted visibility function. However, several of the more recent gloss meters are photoelectric, and some of these use cells whose spectral responses differ quite markedly from that of the average human eye. Where such cells are used, and particularly where these possess appreciable infrared or ultraviolet sensitivity, either the response of the cells should be corrected to approximate visual sensitivity, or the results should not be used as if they were equivalent to visually obtained values.

3. POLARIZATION OF THE LIGHT

Because light specularly reflected at any angle other than normal is, in general, partially polarized, instruments which measure specularly reflected light must be described so that the effect of the optical components upon the state of polarization of the light will be given.

[4] In some few cases, instruments which measure contrast gloss make provision for the use of a selective spectral filter when highly chromatic surfaces are to be measured. It is advisable to do this in order to eliminate chromaticity differences from the photometric field.

Light specularly reflected from glass at about 57° is completely plane-polarized. For many materials having surfaces less smooth than polished glass, the light specularly reflected at this angle is to a major degree also plane-polarized. A method frequently used to measure contrast gloss [15, 22, 25, 46] employs a doubly refracting prism to separate (1) this plane-polarized specular component of reflectance together with half the diffuse reflectance from (2) the other half of the diffuse reflectance, which is plane-polarized at right angles to the specular component. By means of a polarizing prism the intensities of the two separate beams may be compared and a value of contrast gloss obtained (see Ingersoll glarimeter, fig. 9). Instruments which employ this type of contrast measurement give results that usually differ from the contrast-gloss measurements made by other instruments.

VI. SPECULAR GLOSS [5]

In the preceding sections gloss and gloss measurements have been treated in a general way. The six types of gloss will now be considered separately and the devices by which each may be measured described.

Apparent reflectance in the direction of mirror reflection is indicative of specular gloss as shown diagrammatically by figure 4. The shininess of a surface, the brilliance of its reflected high lights, and its specular reflectance are the appearances corresponding to specular glossiness. In this paper the term sheen has been applied to specular gloss at near-grazing angles.

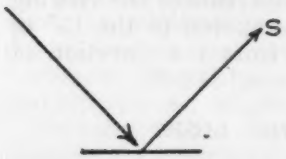

FIGURE 4.—*Specular gloss indicated by apparent reflectance in direction of mirror reflection, S.*

Specular gloss is probably the simplest type of gloss to determine, since its measurement involves finding only the apparent reflectance in the direction of mirror reflection through an instrument aperture which is adapted to the types of surfaces studied. To determine values of specular gloss, permanent standards of apparent reflectance are used to calibrate the photometric device used to make the measurements. Pfund's glossimeter [44], figure 5, uses black glass standards of reflectance and a pyrometer lamp for photometer. This instrument may be adjusted to measure specular gloss at any angle of reflection desired.

Specular gloss measurements are most commonly applied to materials of medium glossiness such as house paints, linoleums, printing ink, etc. On surfaces of low gloss the apparent reflectance in the direction of mirror reflection is often but little larger than the apparent reflectance in other directions. (See curve *M*, fig. 2.) For such surfaces, glossiness is usually better indicated by measures of contrast gloss than by measures of specular gloss. For surfaces of high gloss where the apparent reflectance in the direction of mirror reflection is of the same order of magnitude as the apparent reflectance from perfectly polished surfaces of the same material, one cannot distinguish differences in specular gloss as readily as differences in the distinctness of images

[5] Formerly termed objective gloss [18, 44].

reflected in such surfaces, or differences in bloom, or surface texture. In other words, all surfaces of high specular gloss appear shiny, but small differences in shininess do not attract attention as do the more apparent differences in other gloss qualities.

In designing any device to measure specular gloss it is desirable, on the one hand, to have the angular apertures relatively small so that the instrument receives for measurement only light that is reflected in nearly the exact direction of mirror reflection. On the other hand, surfaces that are warped or wavy furnish a difficult problem when measured by instruments of small aperture, because such surfaces slightly misdirect some of the specularly reflected light so that it misses the narrow aperture and has no part in the resulting measurement. An observer grading surfaces for shininess may see reflected

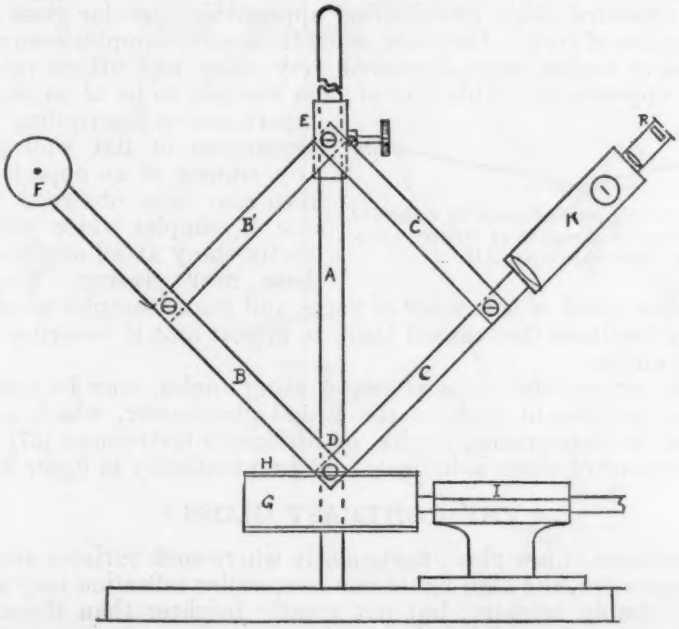

FIGURE 5.—*Pfund's glossimeter—An adjustable, visual, specular-gloss meter* [44].

The sample is bent in the form of a cylinder over *H*.
Light from the source, *F*, is specularly reflected by the test surface and measured by means of a pyrometer lamp, *K*. It is possible to vary the angle at which measurements of specular reflection are made.

high lights displaced because of warpage or waviness, but he discounts these warpage effects in visual grading; consequently an instrument to make the same gradings must discount the effects also. This requires instrument apertures larger than otherwise needed. In designing a specular-gloss meter to measure house paints and other products in the range of medium glossiness, the author [16] found that a source aperture 8.5° in diameter, for an angle of reflection 45°, is satisfactory; the receptor aperture, an artificial pupil, is in this case relatively small.

As explained above, specular gloss measurements are measurements of apparent reflectance employing the direction of mirror reflection and as small an aperture surrounding this direction as the curvature and waviness of surfaces will permit. This makes specular gloss measure-

ments nearly equivalent to measurements of the so-called specular reflectance in that they are less affected by the so-called diffuse reflectance than are other measurements of gloss. For this reason measures of specular gloss are used to compare the gloss characteristics of surfaces of different hues and different lightnesses. In the paint industry, for instance, it is customary to say that white, black, and chromatic paints which have the same vehicular composition and thus have about the same specular reflectance characteristics, have the same gloss. A specular-gloss instrument is well suited to measure them.

VII. SHEEN

The author was only recently introduced to sheen as a type of gloss. Undergoing examination were a number of flat wall paints, none of which appeared shiny or exhibited appreciable specular gloss at the usual angles of view. However, when these same samples were viewed at grazing angles, some appeared very shiny and others remained mat in appearance. This type of gloss was said to be of considerable importance in descriptions of the appearance of flat wall paints. Appearances of an opposite type have also been observed in the case of samples which were distinctly shiny at all angles except those near grazing. Examples have been noted of a number of yarns and paper samples which possessed a fuzziness that caused them to appear mat if viewed at near-grazing angles.

FIGURE 6.—*Sheen indicated by apparent reflectance in direction of mirror reflection at a grazing angle, SH.*

Sheen, or specular gloss at near-grazing angles, may be measured with an instrument such as the Pfund glossimeter, which may be adjusted to near-grazing angles, or Milligan's instrument [37]. The measurement of sheen is indicated diagrammatically in figure 6.

VIII. CONTRAST GLOSS [6]

On surfaces of low gloss, particularly where such surfaces are white or light-colored, the high lights due to specular reflection may appear distinguishably brighter, but not greatly brighter than those areas which do not reflect high lights to the observer. When one views a surface of low glossiness, he seems to appreciate the contrasts between areas reflecting to him specularly and adjacent areas reflecting diffusely. Such a contrast measurement is indicated diagrammatically in figure 7. Contrast-gloss measurements are employed for materials such as paper, flat wall paint, flat lacquer, yarn, etc.

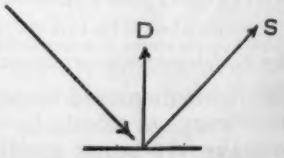

FIGURE 7.—*Contrast gloss indicated by contrast between apparent reflectance in direction of mirror reflection and apparent reflectance in another direction.*

(Possible functions are 1—*D*/*S* and *S*/*D*)

Since the gloss of these materials is low, the excess light due to specular reflectance is widely distributed in the general direction of mirror reflection in a manner characteristic of such surfaces (see curve *M*, fig. 2). For this reason the apertures of instruments used to measure this type of gloss may be

[6] Formerly termed "subjective gloss" [18, 44].

made large if desired. Two contrast-gloss meters are illustrated in figures 8 and 9. In Jones' instrument, figure 8, it may be seen that the apparent reflectance at 45° is photometrically compared with the apparent reflectance at normal viewing.

In the Ingersoll glarimeter, figure 9, the large source-aperture (indicated by the heavy lines, 1 by 1 inch opening, 5¼ inches from the center of the sample) is equivalent to a circular opening approximately 13° in diameter. Since this instrument is generally employed

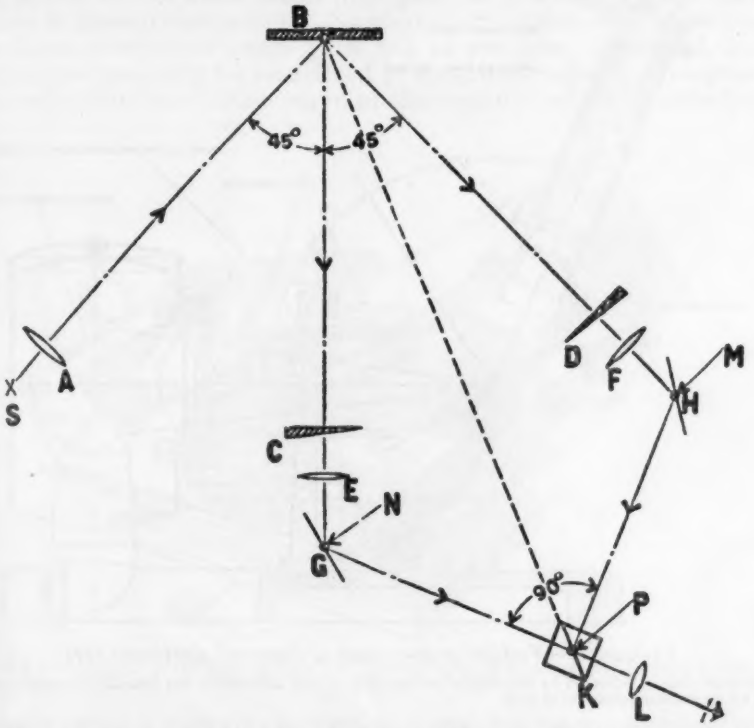

FIGURE 8.—*Diagram of Jones' contrast-gloss meter* [24].

Light from the source, *S*, is incident upon the sample, *B*, at 45°. The apparent reflectance at −45° (diffuse plus specular) is brought into juxtaposition with the apparent reflectance at 0° (diffuse) by means of mirrors, *G* and *H* and the Lummer-Brodhun cube, *K*. The observer can adjust the resulting beams to equal brightness by means of wedges *C* and *D*. The relative brightness of the two reflected beams is given by the inverse ratio of the transmissions of the wedges necessary to bring them to balance in the eyepiece.

throughout the paper industry, it probably enjoys wider use than any other gloss meter. The angle of reflection is 57.5°, the angle of polarization for paper. A doubly refracting Wollaston prism is employed to divide the reflected beam into two beams polarized at right angles for comparison.

IX. ABSENCE-OF-BLOOM GLOSS

By bloom is meant the appearance of haze or smear upon a glossy surface adjacent to a strong specularly reflected high light. Bloom appears most strikingly on dark surfaces which give by reflection

relatively bright images; thus, on a highly polished automobile finish, the smear from a dirty rag or a little oil is plainly visible, particularly when the surface is viewed near an adjacent high light. But little scientific work has been done on this type of gloss, although it seems to have an important influence on appearance.

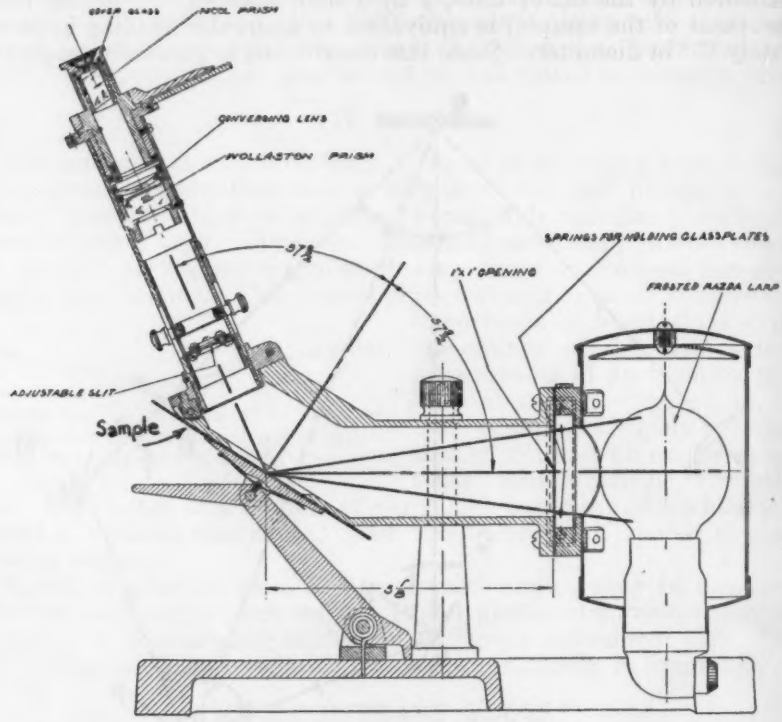

FIGURE 9.—*Vertical cross-section of Ingersoll glarimeter* [22].

Contrast gloss is indicated by the state of polarization of light reflected in the direction of specular reflection for an angle of reflection of 57.5°.

This completes the list of types of gloss which are at present subject to photometric determination. Except for a little work that has been done on metallic surfaces [26], little is known about the quantitative aspect of bloom, which is indicated visually by an excess of apparent reflectance adjacent to the mirror reflection. Whether, for its measurement, it will be desirable to take the difference between apparent reflectance in the direction adjacent to mirror reflection and apparent reflectance in a direction well removed from mirror reflection, or to take some other function of these apparent reflectances, is not yet decided. Different possible magnitudes for indicating bloom are suggested by the diagram in figure 10. In any case, care must be exercised to insure that none of the strongly reflected high light is admitted as bloom.

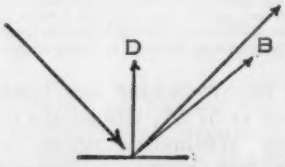

FIGURE 10.—*Bloom indicated by excess of apparent reflectance adjacent to mirror reflection.*

(Possible functions are $B-D$, $1-D/B$, and B/D.)

In figure 11,[7] from [21], is shown a comparison of the power of two surfaces to reflect images of the target used in the gloss lamp. The specimen on the left clearly shows bloom in the dark areas of the image.

X. DISTINCTNESS-OF-REFLECTED-IMAGE GLOSS

Surfaces which give images by reflection are, in general, surfaces of high gloss. Because these images are often the most pronounced feature of the appearance of a surface of high gloss, they are widely used as a criterion in gloss investigations. No photometric method of measuring distinctness-of-reflected-image gloss has as yet been developed, but this type can probably be associated in magnitude with the steepness of the reflection-distribution curve in the region of specular reflection

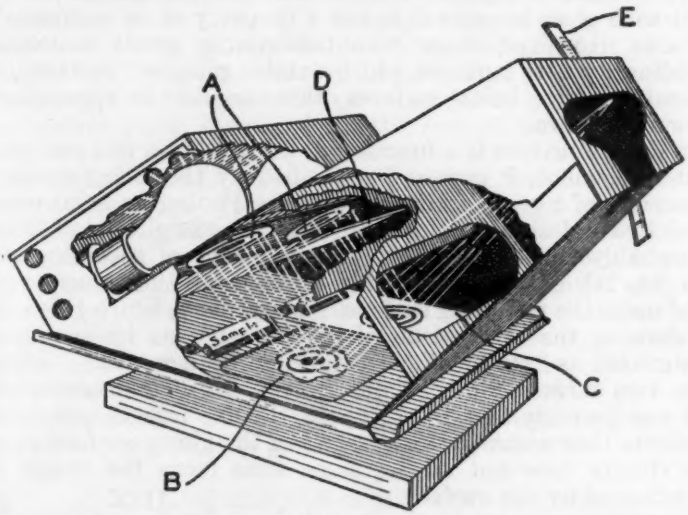

FIGURE 13.—*Hunter gloss comparator for determining distinctness-of-reflected-image gloss [18].*

A pair of target patterns, *A* (reflected images of which may be seen in figs. 1 and 11), are illuminated from behind. An observer views the images of this pair of targets, one of which is reflected by the test surface at *B*, the other by the glass mirror at *C*. The image of the target reflected by the glass mirror is diffused by means of a ground-glass plate, *D*. Motion of this plate toward or away from the target varies the amount of diffusion of the target image, and the position of the glass plate for which the distortion produced by the test surface and that produced by the movable plate appear equal may be determined by an observer and noted on the gloss scale, *E*.

(see curve *P*, fig. 2). So far the methods which have been developed to measure it depend on empirical comparisons.

Probably the method most widely used to reveal gloss differences consists in the comparison of the reflected images which two surfaces give of a window sash. This procedure is usually one of grading the specimens for distinctness-of-reflected-image gloss.

Figure 12[7] illustrates one attempt to establish a distinctness-of-reflected-image gloss scale on a more permanent and reproducible basis than is furnished by the window sash combined with day-to-day comparisons of samples and standard. In 1932 the Detroit Paint Production Club [10] developed a series of standard lacquers of varying degrees of distinctness-of-reflected-image gloss. These lacquers were

[7] Opposite page 23.

arranged on panels and under a lattice frame as illustrated in figure 12. The images reflected by the test sample were compared with those reflected by the members of the series of standards. Lack of permanence of the lacquer standards apparently proved to be the chief obstacle to the success of the scheme.

The Gloss Comparator developed by the author [18], figure 13, is an instrument designed to measure distinctness-of-reflected-image gloss on a continuous scale.

XI. ABSENCE-OF-SURFACE-TEXTURE GLOSS

The term "surface texture" is used to indicate all departures from surface smoothness sufficient in magnitude to be visible to the unaided eye. It has been suggested that surface texture should not be associated with gloss because it is not a property of an elemental area of surface. However, those who customarily grade materials for gloss ordinarily rate surfaces which exhibit pimples, patterns, waviness, scratches, etc., below surfaces otherwise alike in appearance but free of such texture.

Since surface texture is a function of the variation of a surface from element to element, it cannot be specified by the reflection-distribution functions of a given surface test area. Photographs in specularly reflected light (designated in microscopy as "bright-field" illumination) probably furnish the best known means of recording surface texture [18, 21]. In making such a photograph the camera must be focussed upon the reflecting surface. Thus, no. 4, figure 1, is a photograph showing the comparison of images reflected by two surfaces, one designated as "pimpled", the other as "orange peel." Inasmuch as these two surfaces both produced very distinct images when the camera was properly focussed on them, the two images observed here demonstrate that a camera focussed upon the glossy surface to record texture clearly does not at the same time focus the image of the object reflected by the surface.

Many phenomena interesting psychologically are associated with surface texture. There are rivalries for visual fixation between the texture of the surface and the images reflected in the surface. Stereoscopic effects may also be present because of the fact that an observer's two eyes receive images from a single source reflected in two different areas of the image-reflecting surface, with the result that the appearance to one eye is often quite different from the appearance of the same object to the other eye.

In [18] it was suggested that the characteristic of appearance which is commonly known as "depth of finish" might be explained as being due to lack of surface texture. Apparently an object possesses "depth of finish" when the surface of this object presents no texture upon which the one who views the surface may fixate. When the surface of an object is thus nearly invisible, the observer tends to see details of grain or mottling as appearing to be at an unlocated depth within the object.

XII. SUMMARY

The problems of gloss determination differ from many other problems of measurement in that the principal problem seems to be not how to measure the quantities involved, but rather how to determine the best quantities to measure. Gloss is associated with

the ability of objects to reflect light specularly. The structural properties of objects responsible for specular reflection and the glossiness of these objects which results from specular reflection can be described at some length; but the specular reflectance itself, for most objects, cannot be measured because it cannot be separated in any but an approximate way from the diffuse reflectance. Reflection-distribution functions, though complex and cumbersome, offer the only means by which the reflectance properties of surfaces responsible for their glossiness may be completely specified.

Different types of gloss may be classified according to their appearance characteristics. Six types are identified in the present paper, as follows: (1) specular gloss, identified by surface shininess; (2) sheen, identified by surface shininess at grazing angles; (3) contrast gloss, identified by contrasts between specularly reflecting areas of surfaces and other areas; (4) absence-of-bloom gloss, identified by the absence of excess reflection (haze or smear) adjacent to reflected high lights; (5) distinctness-of-reflected-image gloss, identified by the distinctness of images reflected in surfaces; and (6) absence-of-surface-texture gloss, identified by the lack of surface texture and points of fixation which locate the surface. If the designs of existing gloss meters are examined they will usually be found to measure one or more of the above types of gloss. The primary requirement for each of these gloss meters is that, when applied to specimens of the type for which it is intended, it shall give results which correlate satisfactorily with gloss ratings on the same specimens assigned by visual grading. In order to describe gloss meters so that the measurements they make may be reproduced, it is necessary to specify precisely the apparent-reflectance measurement made. Each type of gloss is considered separately and the devices by which each may be measured described. Goniophotometric data provide a basis for the design and improvement of gloss-determining devices.

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WASHINGTON, October 23, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP959

Part of Journal of Research of the National Bureau of Standards, Volume 18
January 1937

A MICROBURETTE FOR TESTING THE ABSORPTIVENESS OF THIN PAPER

By F. T. Carson

ABSTRACT

A microburette, designed to measure and deliver a hundredth milliliter of liquid, is described and illustrated. It consists of a capillary tube, with a sliding index, mounted so that the capillary can be adjusted to any angle of inclination such that the column of liquid in the capillary advances the length of the slider, and thereby displaces a measured volume which then hangs as a small drop from the discharge tip. A mechanism is provided for transferring the pendent drop to the specimen. Although designed particularly for use in the testing of thin absorbent paper, the microburette can probably be adapted to other uses requiring the accurate dispensing of small amounts of liquids.

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I. INTRODUCTION

Absorptiveness is the property of chief importance in some types of paper. Blotting paper has for many years been tested by measuring the absorption time of 1 milliliter of standard ink when delivered in a specified manner on the surface of the paper. Paper towels were formerly tested by this technique for blotting paper, water being substituted for the ink. For a satisfactory test of paper towels, however, a milliliter of water has been found too much, and for still thinner absorbent papers it is out of the question.

In the ordinary use of a paper towel, for example, a small volume of water is spread out thinly over a considerable area of the towel, and is absorbed quickly by penetrating for the most part straight into the sheet. The normal behavior could scarcely be simulated in a test that deposits at a given place so large an amount of water that most of it must be absorbed by spreading out and creeping laterally through the structure of the paper to a considerable distance from the point of origin, as must necessarily occur when a milliliter is poured at a given point on a sheet as thin as a paper towel. Loss by evaporation, when the time for absorption is thus prolonged, is also a source of uncertainty, and in some cases the uncertainty of the test is intensified by part of the water dropping from the underside of the specimen. Improvement in the test has required the application of smaller amounts of water to the specimen. Betterment in this direction,

however, has been somewhat hindered by the difficulty of accurately measuring and delivering much smaller amounts of water at a given point on the paper. Apparatus have been described within the last 3 or 4 years that are capable of delivering 0.1 ml, or somewhat less, with sufficient accuracy to a given position on the specimen,[1] and the use of such apparatus has increased the reliability and meaning of tests of the absorbent quality of paper towels.

For a satisfactory test of yet thinner paper, however, a still smaller amount of water is required. The microburette here described is designed to measure and deliver 10 mm^3, or 0.01 ml, of liquid reproducibly to a predetermined position on the specimen, and is intended to fill the requirement for a means of testing very thin absorbent papers, such as toilet paper, facial tissue, paper napkins, and the like.

II. DESCRIPTION OF THE MICROBURETTE

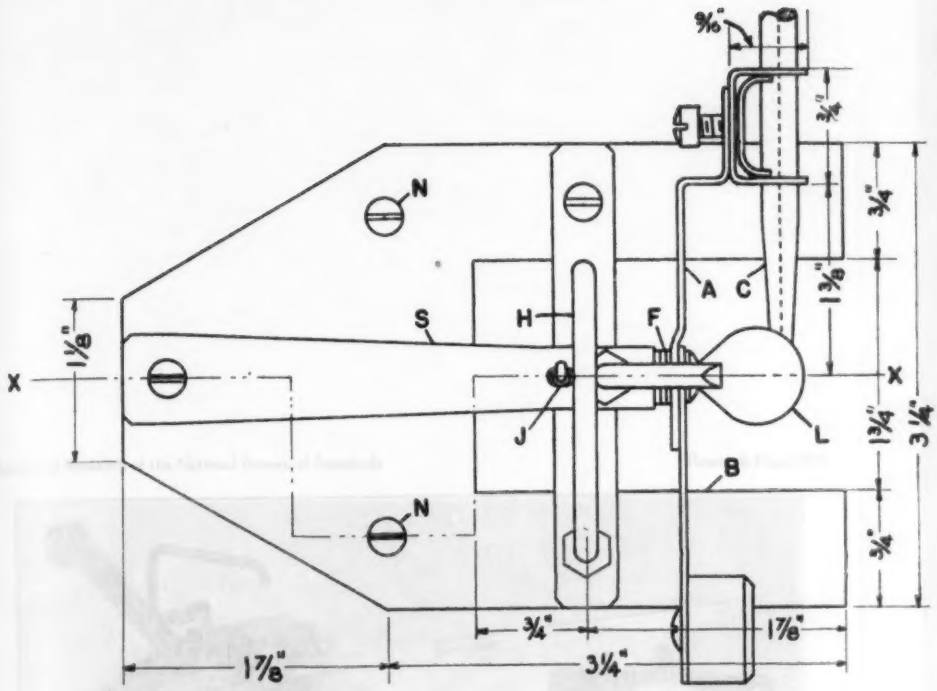
The instrument illustrated in the photograph of figure 1 and the drawing of figure 2 consists of a glass capillary tube, *C*, about 10 inches long, about a quarter of an inch in outside diameter, with a bore about 0.03 inch (¾ mm) in diameter, and having a special mounting adapted to the testing of sheets of paper. One end of the capillary tube is drawn out so that the tip *D* is about 1/16 inch in diameter. It is then bent so that a ¼-inch length at the tip-end is vertical when the capillary tube is inclined at an angle of about 30° with the horizontal. The capillary tube is mounted with two axes of rotation, both of which are horizontal but mutually perpendicular, allowing it to be inclined at a suitable angle and also to be moved vertically without altering the angle of inclination. It is clamped to a counterweighted supporting arm, *A*, that is provided with a friction pivot, *F*, to hold it at any desired angle of inclination from zero to about 60°. Inclining the capillary tube so as to make liquid in it either flow out, or come to rest with the meniscus at any desired point, serves the purpose of the stopcock in the usual form of burette.

Although, ideally, the axis about which the capillary rotates in changing its angle of inclination should pass through the discharge tip, in order that the tip will remain at the same level, regardless of the angle of inclination of the capillary tube, it was not found practical in the construction of the instrument to realize this coincidence of axis and tip, because the discharge tip is almost in contact with the specimen when the liquid is delivered. The axis of the pivot, *F*, is therefore placed slightly above the discharge tip, *D*, yet near enough that the tip will remain at substantially the same level throughout the working range of inclination of the capillary tube.

The microburette is not graduated with fixed reference lines in the customary manner, but is provided with a sliding dual index, *R*, that spans a length of the column of liquid in the capillary corresponding to the volume of 10 mm^3 used in testing the thin absorbent papers. This amount of water when measured from the microburette hangs as a small drop from the delivery tip and slightly above the specimen of paper to be tested.

To provide a mechanism for bringing the pendent drop into contact with the paper, the microburette is fastened to the base through the

[1] Carson and Worthington, Paper Trade J. 95, TS188 (1932).
Reese and Youtz, Paper Trade J. 100, TS67 (1935).
Krogh, J. Ind. Eng. Chem., Anal. Ed. 7, 130 (1935).



A-COUNTERWEIGHTED SUPPORT
B-BASE
C-CAPILLARY
D-DISCHARGE TIP
F-FRICTION DISKS
H-HANDLE
J-UPPER STOP
K-LOWER STOP
L-LEVER
M-TEST SPECIMEN
N-HINGE BOLT
P-PLATE
R-SLIDING DUAL INDEX
S-LEAF SPRING
T-FILLING THIMBLE

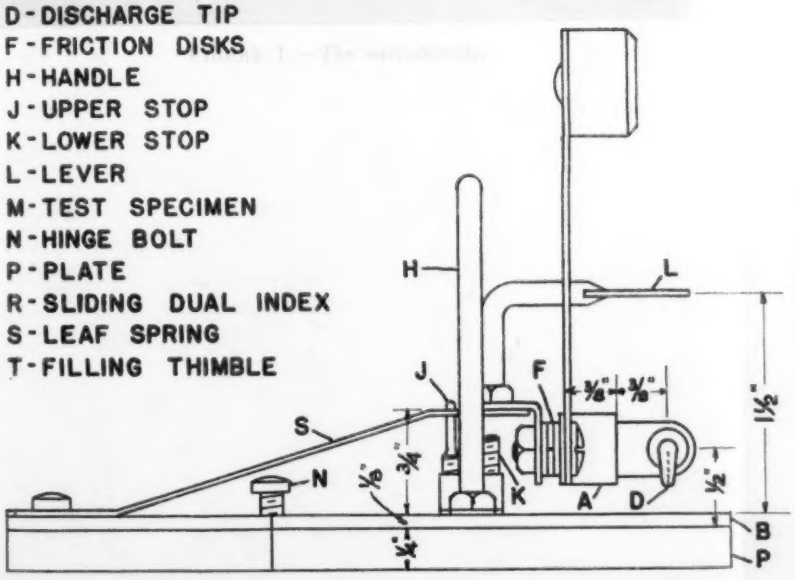
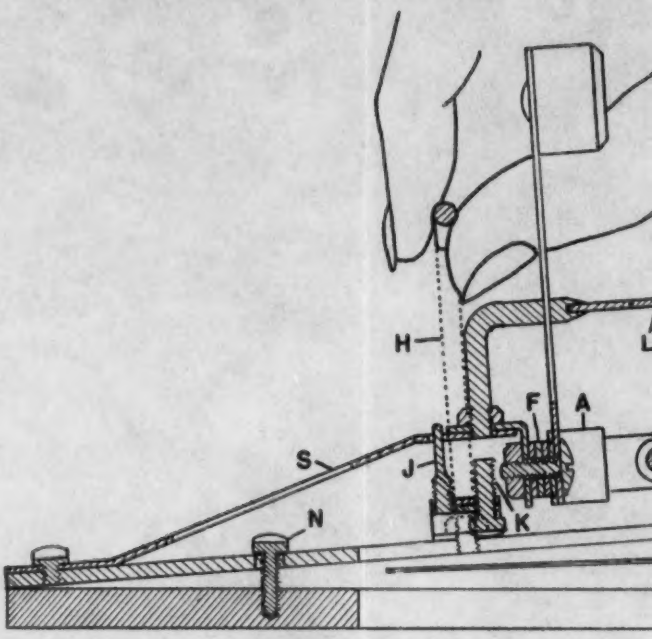
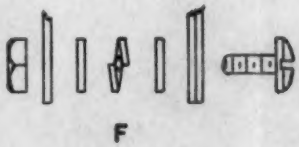
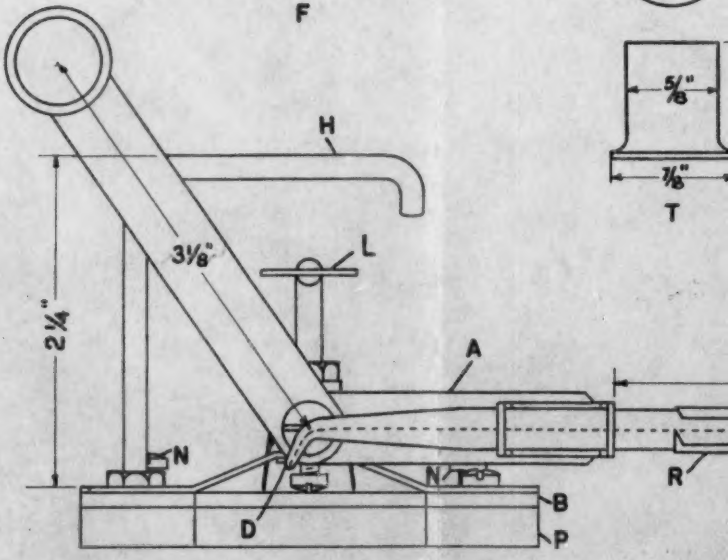


FIGURE 2.—*Detailed*

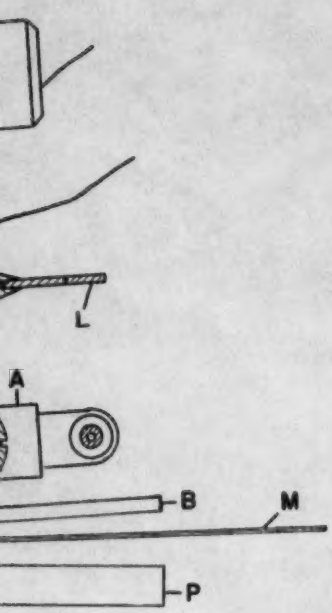


SECTION X—X
INSTRUMENT OPEN FOR INSERTION OF TEST

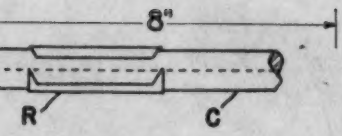




2.—*Detailed drawing of the microburette.*



TEST SPECIMEN



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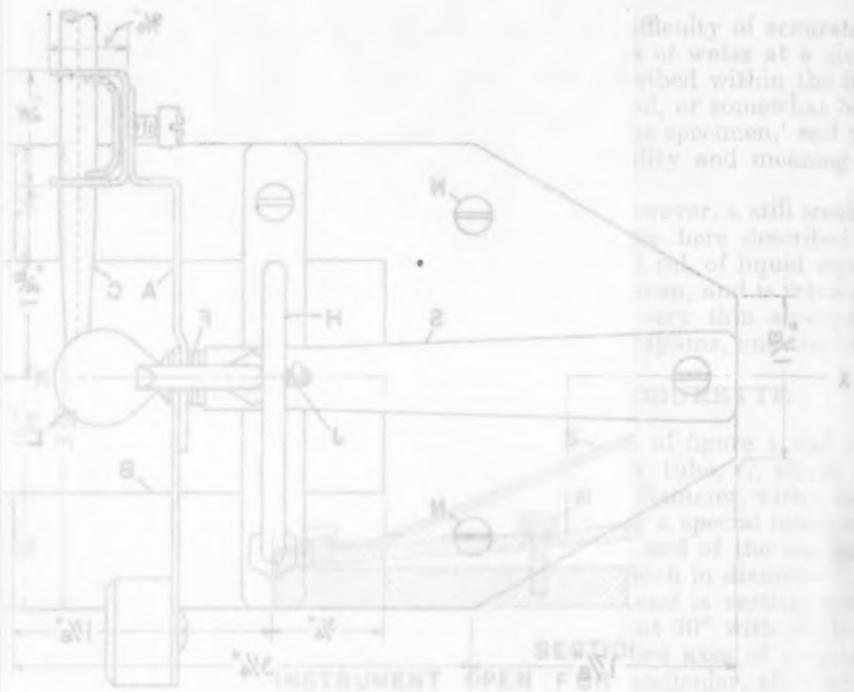

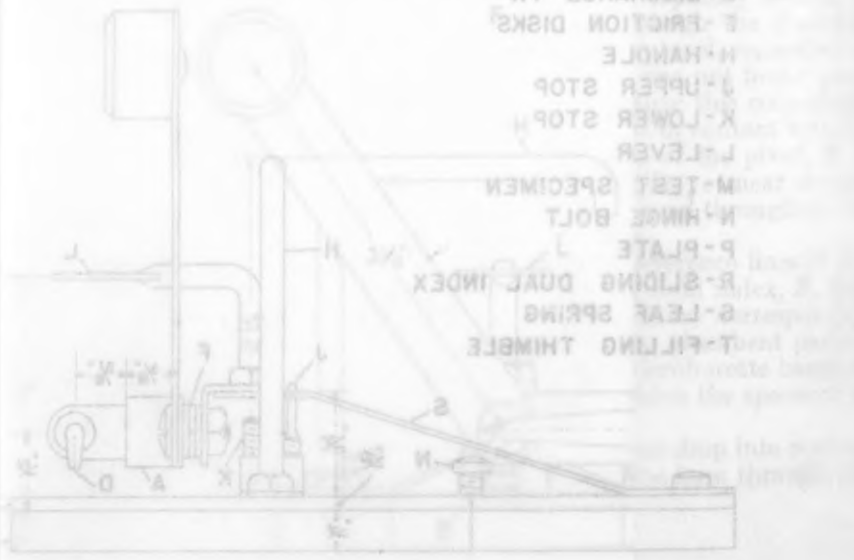

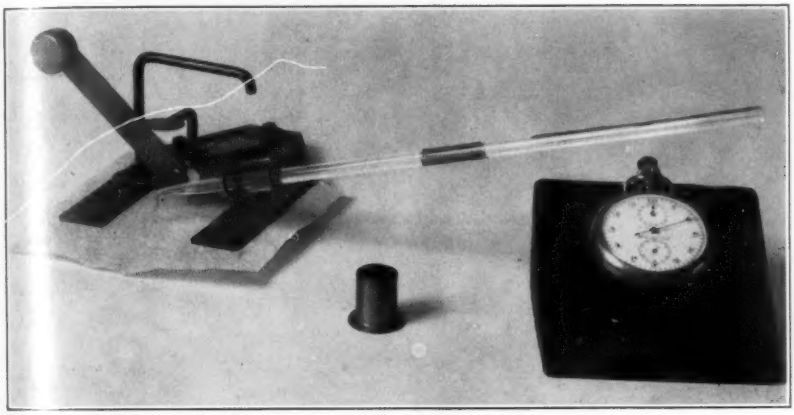

FIGURE 1.—*The microburette.*

medium of a stiff leaf spring, *S* (fig. 2), provided with adjustable stops, *J* and *K*. While the drop is being measured the spring rests against the upper stop, *J*, which is so adjusted that the discharge tip is held about 3/16 inch above the specimen. When, however, the spring is pressed down against the lower stop, *K*, by depressing the lever, *L*, the capillary tube is lowered as a whole without altering the angle of inclination, the discharge tip being brought within about 1/16 inch of the specimen. This adjustment allows the drop to touch the specimen without being distorted objectionably. The drop of water

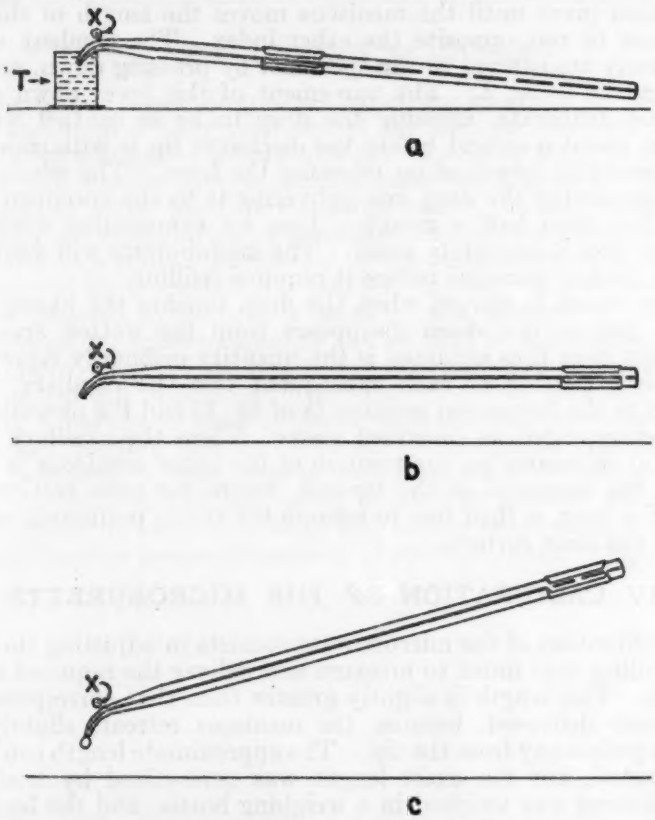

FIGURE 3.—*Diagram of filling position (a), starting position (b), and delivery position (c) of the microburette.*

The axis of inclination is at *X*.

adheres to the paper and is pulled away from the tip of the microburette as the lever is released.

The specimen, *M*, is clamped in place below the discharge tip by the weight of the instrument. It is held between the base, *B*, of the mounting and an underlying plate, *P*, similar to the base, *B*, and hinged to it by means of screws, *N*, that extend through slots in the base, *B*, and allow the plate, *P*, to fall away slightly from the base when the instrument is lifted by the handle, *H*. The clamp is thus opened for inserting the specimen, *M*.

III. OPERATION OF THE MICROBURETTE

The capillary tube is filled in position *a* of figure 3. The tip, is immersed in distilled water [2] contained in the thimble, *T*, and the other end is lowered, whereupon the water siphons over and fills the capillary. All water is then wiped from the exterior with absorbent cloth or paper.

The capillary tube is next moved to the horizontal position (*b* of fig. 3) and the outer index of the slider, *R*, is moved into coincidence with the meniscus. The microburette is then rotated (*c* of fig. 3) on the friction pivot until the meniscus moves the length of the slider and comes to rest opposite the other index. The pendent drop is immediately transferred to the specimen by pressing down, and then releasing, the lever, *L*. The movement of this lever down and up should be deliberate, allowing the drop to be in contact with the specimen about a second before the discharge tip is withdrawn from it, and avoiding vibration on releasing the lever. The whole operation of measuring the drop and delivering it to the specimen should require less than half a minute. Loss by evaporation during this length of time is negligibly small. The microburette will deliver five or more 10-mm^3 portions before it requires refilling.

A stop watch is started when the drop touches the paper, and is stopped just as the sheen disappears from the wetted area. The absorption time thus obtained is the quantity ordinarily reported.

At the beginning of each subsequent test the capillary tube is returned to the horizontal position (*b* of fig. 3) and the operations are thereafter repeated as described above. When the capillary tube is horizontal or nearly so, the position of the outer meniscus is stable, because the meniscus at the tip-end, where the cross section of the bore is the least, is then free to assume the stable position in which it presents the least surface.

IV. CALIBRATION OF THE MICROBURETTE

The calibration of the microburette consists in adjusting the length of the sliding dual index to measure and deliver the required amount of liquid. This length is slightly greater than that corresponding to the volume delivered, because the meniscus retreats slightly after the drop pulls away from the tip. The approximate length can readily be estimated, but the exact length was determined by trial. The drop delivered was weighed in a weighing bottle, and the length between temporary marks on a slider was adjusted until the average of several successive trials corresponded to the required amount of water. When the exact length had been determined, a metal slider was made with two fixed indices separated by the correct distance.

The uncertainty in a particular delivery is around 5 percent, but the average uncertainty in several successive deliveries is small. An example of the performance of the microburette, calibrated to deliver 10 mm^3, is shown in table 1. Since it is customary to make at least 10 tests per sample, the error resulting from uncertainty in the amount of water delivered is small in the mean value for the sample.

[2] Although distilled water is not necessary to the testing of the absorptiveness of paper, its use will help to avoid difficulty in filling the capillary, since otherwise the bore is likely to become gradually encrusted with a deposit from impure water that will make it difficult to wet. In an extremity, of course, filling can be effected by suction on the end with a medicine-dropper bulb. Likewise, to prevent fouling with organic matter, the capillary should be emptied after use. Emptying is easily effected by holding a piece of blotting paper against the discharge tip.

TABLE 1.—*Data showing the reproducibility in several successive trials*

Trial number	Volume delivered	Error	Trial number	Volume delivered	Error
	mm³	*Percent*		mm³	*Percent*
1	9.7	−3	7	9.6	−4
2	9.7	−3	8	10.0	0
3	10.4	+4	9	10.2	+2
4	10.0	0	10	10.1	+1
5	10.5	+5			
6	10.1	+1	Average	10.03	+0.3

V. CONCLUDING REMARKS

Although the 10-mm³ drop deposited on the specimen by the microburette results in a fairly good test of the absorptiveness of the class of papers for which the instrument was designed, it might be desirable to use a still smaller drop in testing some tissue papers. Likewise, in the test of paper towels for absorptiveness, the conditions of absorption in use would be better simulated and other advantages would result, such as a shorter test period, if the customary 0.1 ml of water were replaced by a considerably smaller volume. The microburette, which is designed to dispense a tenth of this amount, is, therefore, recommended for consideration in the revision of specifications or in further improvement of the test of the absorptiveness of paper towels.

The instrument which has been described was designed for the testing of a particular kind of paper, and the test has been used in Federal specifications for about 3 years. Although designed to meet a specific requirement, the microburette can probably be easily adapted to the measurement of somewhat greater or smaller volumes, to the dispensing of various liquids, and to the requirements of other uses involving the precise dispensing of small amounts of liquids.

WASHINGTON, October 27, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP960

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

THERMAL EXPANSION OF CEMENTED TUNGSTEN CARBIDE

By Peter Hidnert

ABSTRACT

This paper gives data on the linear thermal expansion of tungsten carbide-cobalt mixtures containing about 6 and 13 percent of cobalt. These products are called "cemented tungsten carbide" or Carboloy in the United States and Widia in Germany.

The expansion curves of four samples of cemented tungsten carbide are shown in figures 1 and 2. Table 2 gives coefficients of expansion for various temperature ranges between 20 and 400° C. The average coefficient of expansion of cemented tungsten carbide containing 5.9 percent of cobalt, increases from 4.4×10^{-6} for the range between 20 and 60° C to 5.9×10^{-6} for the range between 300 and 400° C. The average coefficients of expansion of the samples of cemented tungsten carbide containing from 12.9 to 13.2 percent of cobalt, increase from 5.0×10^{-6} for the range between 20 and 60° C to 6.7×10^{-6} for the range between 300 and 400° C. For the range from 20 to 400° C, the average coefficients of expansion of the samples of cemented tungsten carbide containing about 13 percent of cobalt are 15 percent greater than the coefficient of expansion of the cemented tungsten carbide containing about 6 percent of cobalt.

Figure 3 shows that the rates of expansion of the samples of cemented tungsten carbide increase linearly with temperature. The rates of expansion of the cemented tungsten carbide containing 13.0 percent of cobalt are greater than the rates for the carbide containing 5.9 percent of cobalt. The rates of expansion of the samples of cemented tungsten carbide are greater than the rates of expansion of tungsten and considerably less than the rates of expansion of cobalt.

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I. INTRODUCTION

Becker [1][1] determined by an X-ray method [2], the coefficients of expansion of two tungsten carbides α–W_2C and WC. He reported the following coefficients of linear expansion: For α–W_2C, a–axis 1.2×10^{-6} and c–axis 11.4×10^{-6} per degree centigrade between 20 and 2,400° C; for WC, a–axis 5.2×10^{-6}, and c–axis 7.3×10^{-6} per degree centigrade between 20 and 1,930° C.

Agte [3] in 1930 reported 5×10^{-6} for the coefficient of linear expansion of a tungsten carbide-cobalt mixture containing 5 percent of

[1] Numbers in brackets refer to references at end of paper.

cobalt, for the range from 20 to 1,000° C. Hidnert [4] in the same year reported coefficients of linear expansion of two samples of tungsten carbide-cobalt mixtures containing about 13 percent of cobalt. The average coefficients of expansion of these two samples increased from 5.0×10^{-6} for the range between 20 and 60° C to 6.0×10^{-6} for the range between 20 and 400° C. The present paper gives additional data on the linear thermal expansion of tungsten carbide-cobalt mixtures containing approximately 6 and 13 percent of cobalt. These mixtures are called "cemented tungsten carbide" or Carboloy in the United States and Widia in Germany.

Data on the thermal expansion of cemented tungsten carbide, which is used in industry, should be available. This material, which belongs to the class of superhard materials, is used extensively in cutting tools. Cemented tungsten carbide has been used for cutting materials such as alloy steels, bronzes, hard rubbers, and fibrous materials. In cutting operations, temperature changes affect the tool and the work. This material, because of its low thermal expansion, undergoes small dimensional change during such operations as cutting and grinding. A knowledge of the thermal expansion of cemented tungsten carbide will be of assistance wherever this alloy may be assembled in instruments constructed of materials having different expansions.

II. MATERIALS INVESTIGATED

Cemented tungsten carbide may be made from an intimate mixture of powdered tungsten carbide (*WC*) and cobalt prepared by ball milling. Hoyt [5] stated that "The mold is constructed to permit electrical heating and is provided with a top and a bottom plunger for applying the pressure. The heating is accomplished either by passing a current through the plungers, using top and bottom electrodes, or by passing current through the mold proper by using side electrodes."

Table 1 gives the dimensions and the cobalt contents of four samples of cemented tungsten carbide, which were investigated. Samples *1374I* and *1375I* were purchased in 1929 from Carboloy Co., Inc., New York, N. Y. Samples *1399I* and *1400I* were furnished to this Bureau, in 1930, by General Electric Co., Schenectady, N. Y.

TABLE 1.—*Dimensions and cobalt contents of samples of cemented tungsten carbide*

Sample	Length	Diameter	Cobalt content
	mm	mm	*Percent*
1374I	7.0	3.8	13.2
1375I	8.7	4.6	13.0
1399I	9.5	6.6	12.9
1400I	9.3	6.8	5.9

III. APPARATUS

On account of the small amounts of cemented tungsten carbide available, the interference method [6] of measuring thermal expansion was employed. At each observation, the temperature was kept constant for a sufficiently long time to make certain that the sample had attained temperature equilibrium.

IV. RESULTS

Since a preliminary test on a sample of cemented tungsten carbide indicated that it oxidized between 430 and 480° C, the expansion tests were not carried above 400° C (approximately). Figures 1 and 2 show the observations that were obtained on heating and cooling. Each expansion curve was plotted from a different origin in order to display the individual characteristics of each curve.

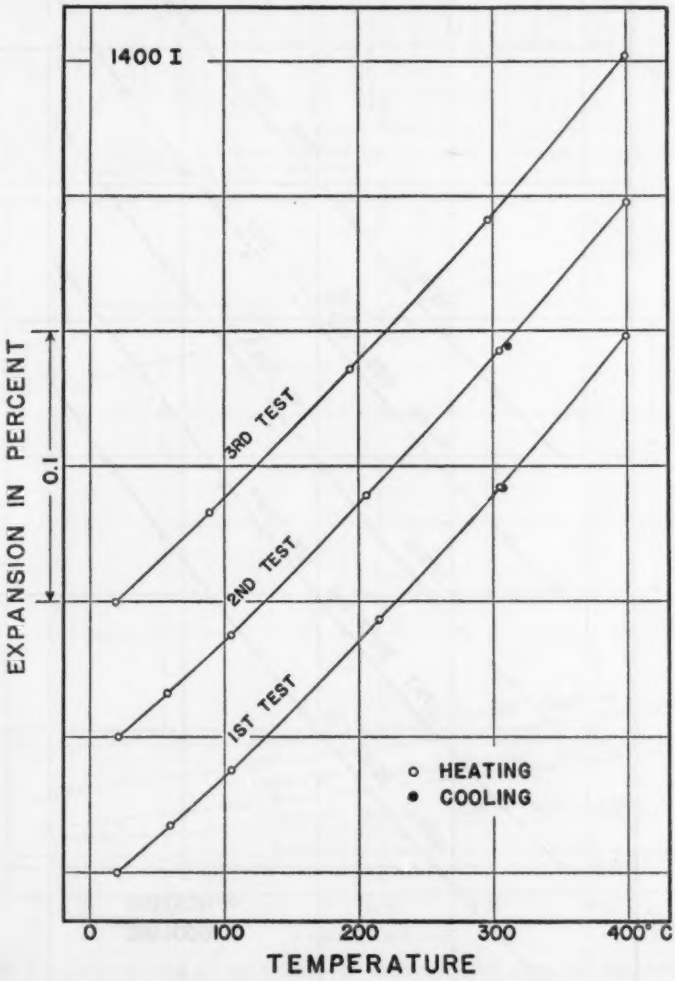

FIGURE 1.—*Linear thermal expansion of sample of cemented tungsten carbide (5.9 percent of cobalt).*

Table 2 gives coefficients of expansion which were obtained from the expansion curves shown in figures 1 and 2. The coefficients of expansion increase with temperature. For the range from 20 to 400° C, the coefficients of expansion of the samples containing about 13 percent of cobalt are 15 percent greater than the coefficient of expansion of the sample containing about 6 percent of cobalt.

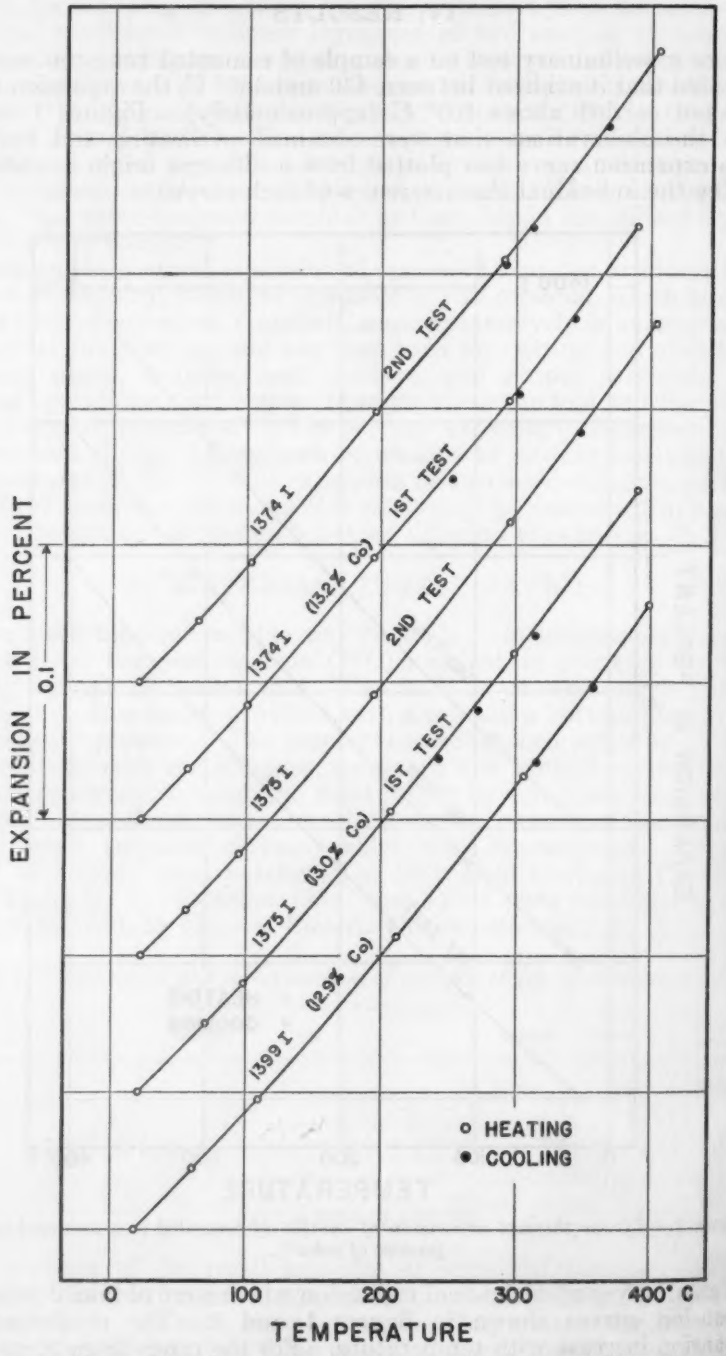

FIGURE 2.—*Linear thermal expansion of three samples of cemented tungsten carbide (12.9 to 13.2 percent of cobalt).*

TABLE 2.—*Average coefficients of linear expansion of cemented tungsten carbide*

Sample	Cobalt content	Test	Average coefficients of expansion per degree centigrade									Change in length after heating and cooling [a]
			20 to 60° C	60 to 100° C	100 to 200° C	200 to 300° C	300 to 400° C	20 to 100° C	20 to 200° C	20 to 300° C	20 to 400° C	
	percent		×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Percent*
1400*I*.....	5.9	1	4.5	4.5	5.0	5.4	5.9	4.5	4.8	5.0	5.2	+0.05
		2	4.4	4.6	5.1	5.4	5.8	4.4	4.8	5.0	5.2	
		3	----	----	5.1	5.4	6.0	4.7	4.9	5.1	5.3	----------
1399*I*.....	12.9	1	5.0	5.2	5.7	6.2	6.7	5.2	5.5	5.7	6.0	+.04
1375*I*.....	13.0	1	5.0	5.3	5.7	6.3	6.5	5.2	5.5	5.8	6.0	−.06 [b]
		2	4.9	5.4	5.8	6.3	6.7	5.2	5.5	5.8	6.0	
1374*I*.....	13.2	1	5.2	5.4	5.7	5.8	6.8	5.3	5.5	5.6	5.9	+.04 [b]
		2	5.1	5.4	6.0	5.9	6.7	5.2	5.6	5.7	6.0	

[a] The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length.
[b] Change in length after 2 heating and cooling cycles.

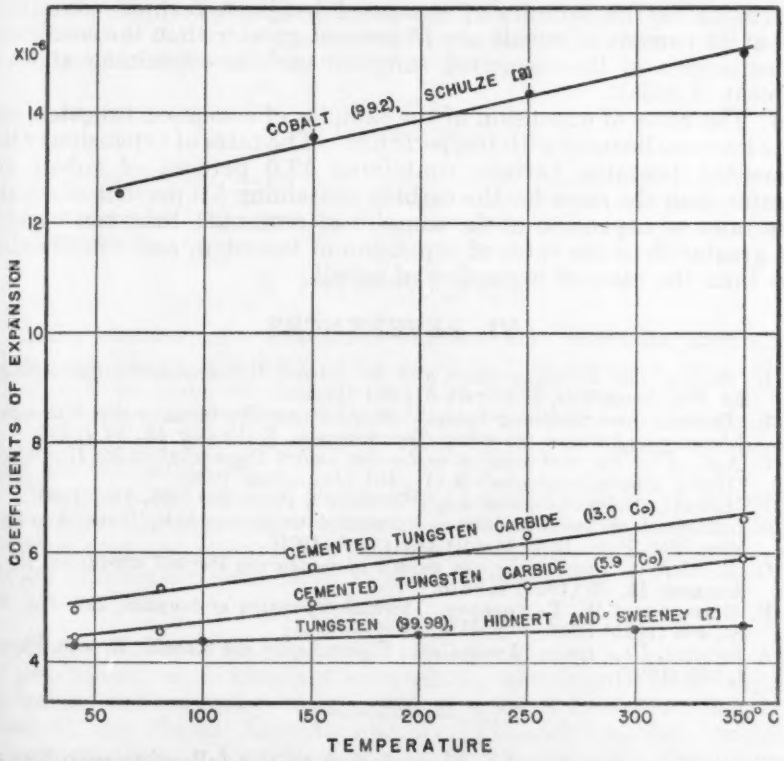

FIGURE 3.—*Comparison of coefficients of expansion or rates of expansion of two samples of cemented tungsten carbide, tungsten, and cobalt.*

Figure 3 shows the coefficients of expansion or rates of expansion of two samples of cemented tungsten carbide containing 5.9 and 13.0 percent of cobalt. Data on tungsten by Hidnert and Sweeney [7] and on cobalt by Schulze [8], are included for comparison. This figure shows that the rates of expansion of the samples of cemented tungsten carbide increase linearly with temperature. The rates of expansion of the cemented tungsten carbide containing 13.0 percent

of cobalt are greater than the rates for the carbide containing 5.9 percent of cobalt. The rates of expansion of the samples of cemented tungsten carbide are greater than the rates of expansion of tungsten, and considerably less than the rates of expansion of cobalt.

V. CONCLUSIONS

1. The average coefficient of expansion of cemented tungsten carbide containing 5.9 percent of cobalt increases from 4.4×10^{-6} for the range between 20 and 60° C to 5.9×10^{-6} for the range between 300 and 400° C.

2. The average coefficients of expansion of the samples of cemented tungsten carbide containing from 12.9 to 13.2 percent of cobalt, increase from 5.0×10^{-6} for the range between 20 and 60° C to 6.7×10^{-6} for the range between 300 and 400° C.

3. For the range from 20° to 400° C, the average coefficients of expansion of the samples of cemented tungsten carbide containing about 13 percent of cobalt are 15 percent greater than the coefficient of expansion of the cemented tungsten carbide containing about 6 percent of cobalt.

4. The rates of expansion of the samples of cemented tungsten carbide increase linearly with temperature. The rates of expansion of the cemented tungsten carbide containing 13.0 percent of cobalt are greater than the rates for the carbide containing 5.9 percent of cobalt. The rates of expansion of the samples of cemented tungsten carbide are greater than the rates of expansion of tungsten, and considerably less than the rates of expansion of cobalt.

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The author expresses his appreciation to the following members of the staff of the National Bureau of Standards: H. W. Bearce, W. Souder and H. S. Rawdon, for valuable suggestions; J. L. Hague for the determinations of the cobalt contents of the samples of cemented tungsten carbide and J. Burks for assistance in the preparation of the figures.

WASHINGTON, October 29, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP961

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

DETERIORATION OF CHROMIC ACID BATHS USED FOR ANODIC OXIDATION OF ALUMINUM ALLOYS

By R. W. Buzzard and J. H. Wilson

ABSTRACT

Commercial practice has shown that chromic acid baths for anodizing aluminum eventually fail. This failure, which had heretofore been attributed to other causes, has been shown to be caused by dissolved aluminum. The addition of chromic acid to the bath at regular intervals to maintain a constant pH is suggested as a means of improving bath control.

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I. INTRODUCTION

In the commercial operation of chromic acid baths for anodizing [1] aluminum alloys, the baths eventually fail to produce good films. When inferior films are first formed, the effectiveness of the solution may be temporarily restored by arbitrary additions of chromic acid, but a condition may be reached when further additions of chromic acid are without effect.

This report summarizes the results of a study made to determine the essential changes that occur in the continued operation of the chromic acid anodizing baths and the conditions that must be controlled to maintain such baths in effective operation.

II. PROCEDURE

Hexavalent and trivalent chromium, aluminum, iron, copper, chlorides, and sulphates were found in a spent bath that had been used at the Naval Aircraft Factory, Philadelphia, for anodizing aluminum alloys. Experiments with freshly prepared chromic acid baths, to which were added, singly, amounts of the above substances slightly in excess of those found in the spent bath, indicated that failure of the bath was caused by a decrease in the content of hexavalent chromium or an increase in that of aluminum. Iron and sulphates, even when added in considerable excess over the amounts found in the spent bath, did not adversely affect the bath performance.

[1] The term "anodizing" is now commonly used in industry to refer to the production of a protective film on the surface of a metal, as aluminum, by making it the anode of a suitable electrolytic cell.

Additions of chloride (which would not be present in normal bath operation) caused readily observable attack at both electrodes.

On the basis of these preliminary tests, the investigation was confined to a study of the changes in the concentration of the principal constituents; namely, hexavalent chromium, trivalent chromium, and aluminum.

The rate at which the chromic acid bath deteriorates when used was determined by anodizing sheets of *17ST* aluminum alloy (dur-

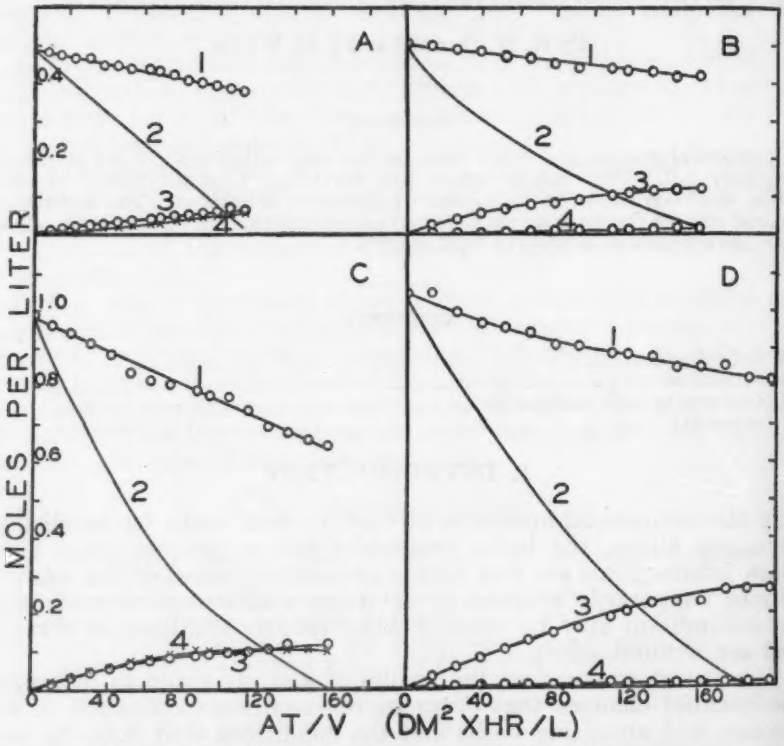

FIGURE 1.—*Change in the concentration of principal constituents in anodizing baths with continued use.*

A. 5 percent of chromic acid, large cathode.
B. 5 percent of chromic acid, small cathode.
C. 10 percent of chromic acid, large cathode.
D. 10 percent of chromic acid, small cathode.
1. Hexavalent chromium.
2. Free chromic acid.
3. Aluminum.
4. Trivalent chromium.

alumin), each 10 by 10 cm, in small glass battery jars varying in capacity from 4 to 7 liters. Iron cathodes were used, the areas of which were varied in order to determine the effect of the ratio of anode to cathode area upon the rate of deterioration of the bath. Chromic acid solutions with concentrations of 3, 5, and 10 percent (0.3, 0.5, and 1.0*M*) were used. The anodizing was conducted at 40° C. with a constant bath potential of 40 volts for periods of about 7 hours. The anodes were renewed hourly, and a sample of the solution was removed from the bath after each 25 hours of operation and analyzed. The baths were operated until a heavy sludge formed.

III. CHANGES IN BATH COMPOSITION

In figure 1 is shown the rate of change of concentration of the constituents with continued use of the bath. The molar concentration, M, of each of the constituents of the solution is there plotted against the value of AT/V, in which A is the anode area treated (in these experiments $A=2$ $_{dm}{}^2$), T is the total time of the use of the bath (in hours), and V is the volume of the bath (in liters).

The product of the total time the bath has been used and the average surface area treated is approximately proportional to the total quantity of electricity passed. In practical operation, the current density is not measured, but the operating conditions are maintained by bringing the voltage to the desired maximum, which is maintained the greater part of the anodizing period For practical purposes it may be assumed that the average current density was approximately constant during the greater part of the anodizing period. Allowance has been made for baths of different volume by dividing AT by the volume of the bath. In effect, therefore, AT/V is proportional to the number of ampere-hours per liter of solution.

In baths A and B (fig. 1) the chromic acid had an initial concentration of $0.5M$ (5 percent) and in baths C and D, twice this concentration. The cathode areas in baths A and C were 50 times those in B and D.

It was found that the concentration of hexavalent chromium (curve 1, fig. 1) decreased, while that of aluminum and trivalent chromium (curves 3 and 4, fig. 1) increased. In baths B and D, with small cathode areas and correspondingly high cathode current densities, the increase of trivalent chromium was almost negligible. This difference is consistent with the fact that reduction of chromium from the hexavalent to the trivalent state is relatively greater at low than at high current densities.

The effective or available chromic acid has been expressed as free chromic acid by Haring and Barrows,[2] in discussing the effective concentrations of chromic acid for chromium plating; and Kasper [3] has shown that chromium dichromate, $Cr_2(Cr_2O_7)_3$, is formed by the reduction of chromic acid. On the assumption that a similar compound of aluminum, $Al_2(Cr_2O_7)_3$, is formed by the reaction between chromic acid and aluminum, the free chromic acid may be calculated as follows: free chromic acid, $(M)=Cr^{VI}$, $(M)-3[Cr^{III}$, $(M)+Al$, $(M)]$. (M=molar concentration.)

The changes in concentration of free chromic acid during the effective life of each bath are shown in curves 2 of figure 1. In the freshly prepared baths the concentrations were the same as those of the hexavalent chromium. With continued operation of the bath the content of free chromic acid decreased steadily toward zero. Anodic films produced when the baths were in the latter condition had inferior corrosion resistance. It was also found that, as the baths became depleted in free chromic acid, a precipitate was formed, which finally collected as a heavy sludge in the bottom of the bath. This sludge was probably a basic chromate of chromium and aluminum. The more rapid increase in the aluminum concentration in baths B and D, as

[2] H. E. Haring and W. P. Barrows, *Electrodeposition of chromium from chromic acid baths.* Tech. Pap. BS 21, 413 (1926-27) T346.

[3] Charles Kasper, *The structure of the chromic acid plating bath, the theory of chromium deposition.* BS J. Research 9, 353 (1932) RP476.

compared to that in baths *A* and *C*, indicates that the presence of trivalent chromium in *A* and *C* retarded the dissolving of aluminum. The aluminum dissolves more rapidly with the higher initial concentration of chromic acid (fig. 2).

Numerous experiments indicate that successful anodization of aluminum depends upon the presence of free chromic acid. One very important difference between chromium dichromate and aluminum dichromate is that the trivalent chromium of chromium dichromate can be reoxidized at the anode to the hexavalent state, thereby releasing four moles of hexavalent chromium for each mole of trivalent chromium oxidized. This probably explains the fact that good films have been produced experimentally in anodizing baths composed essentially of chromium dichromate. On the other hand, this cannot be done with aluminum dichromate, and there is no effective method of removing aluminum from such baths. Hence, the aluminum permanently removes the hexavalent chromium from its free state.

In these anodizing solutions the favorable operating conditions vary with the initial concentration of chromic acid. A 3-percent (0.3*M*)

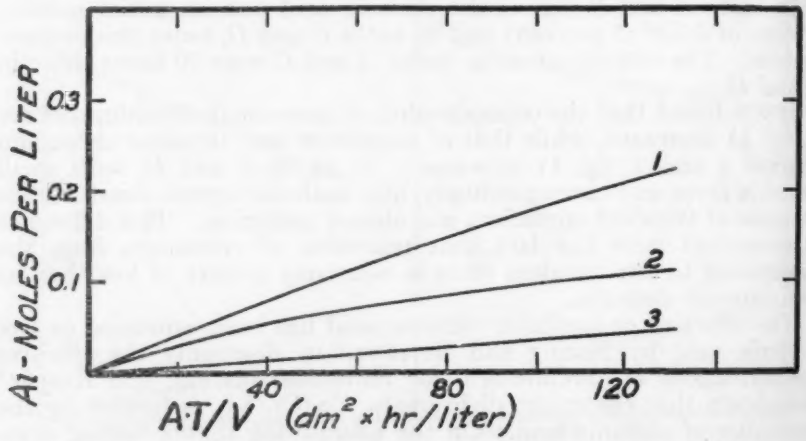

FIGURE 2.—*Rate of solution of aluminum in chromic acid on anodizing.*

1. 10-percent chromic acid bath.
2. 5-percent chromic acid bath.
3. 3-percent chromic acid bath.

chromic acid bath requires a definite voltage cycle to produce the best film, whereas 5- and 10-percent (0.5 and 1.0*M*) chromic acid baths anodize more successfully at constant voltage. Lower temperatures and voltages may be used with the 10-percent chromic acid (1.0*M*) bath, and under proper operating conditions the time required for coating may be shortened. As the free chromic acid concentration of the solution decreases, the operating conditions must be altered to suit the new conditions of concentration, or else additions of chromic acid must be made to maintain the initial concentration of free acid.

Because free chromic acid is the determining factor in anodizing solutions, its concentration should be known and controlled. It is possible to maintain it at any desired concentration by making relatively simple determinations, as pH measurements. In figure 3 is shown the relation of the pH (determined by a glass electrode) to the free chromic acid concentration as the latter varies from that of a

freshly prepared 10-percent bath to that of a completely broken down bath with no free chromic acid. It was found experimentally that by making frequent pH determinations and adding chromic acid in accordance with figure 3 to restore the original or any other desired pH, the free chromic acid concentration of the bath can be maintained constant, and uniformly good films can be obtained.

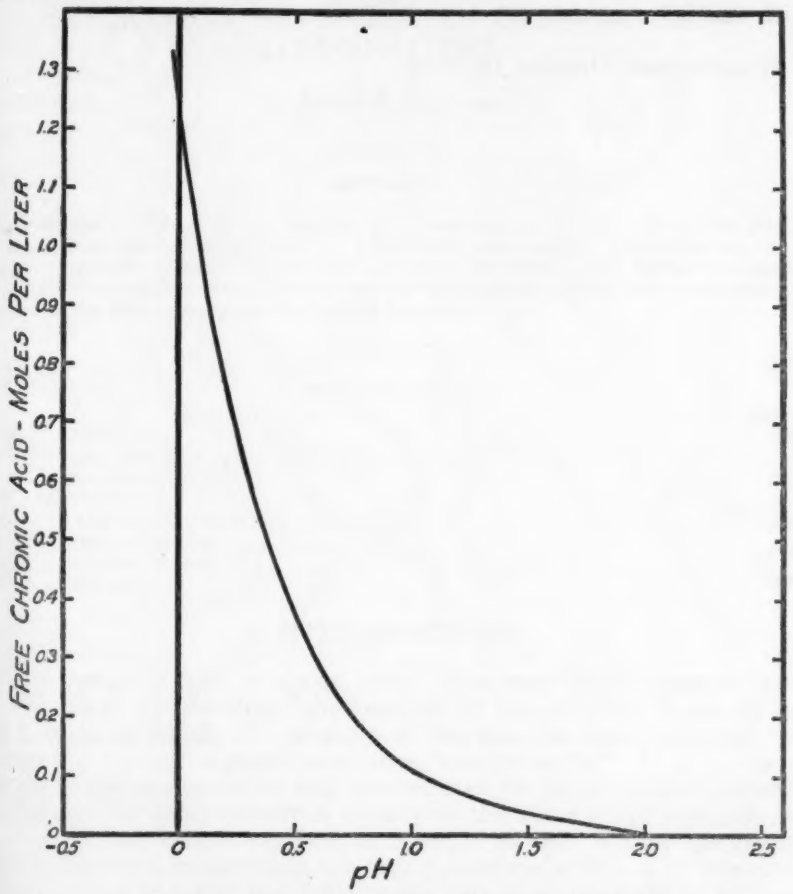

FIGURE 3.—*Relation of* pH *to free chromic acid.*

IV. SUMMARY

1. Failure of anodizing baths as a result of use is caused principally by the neutralization of free chromic acid by aluminum.

2. The true criterion of the working condition of the bath is the concentration of free chromic acid. pH measurements with a glass electrode furnish a convenient means for determining and controlling the condition of the bath.

3. The useful life of an anodizing bath may be greatly prolonged by maintaining the solution at the required pH. The free chromic acid content is maintained at the desired value by adding chromic acid to the bath in accordance with the pH values.

4. Experience has shown that maintenance of the bath at a constant pH insures the obtaining of anodic oxide films that are very uniform in character.

The authors express their sincere thanks to Dr. William Blum and Dr. Richard M. Wick for their many helpful suggestions in connection with this investigation.

WASHINGTON, October 19, 1936.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP962

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

SATURATION BY WATER IN GAS ANALYSIS COMPENSATORS

By Joseph R. Branham

ABSTRACT

The effects of diffusion, convection, and evaporation of water from the glass surface in the compensators used in volumetric gas-analysis apparatus are discussed. The data presented show that serious errors result under certain common temperature conditions when, for the sake of thermal similarity, the compensator used is of the same shape as the bulbed burette.

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I. INTRODUCTION

In volumetric gas analysis, over mercury, measurements are usually made by observing the position of the mercury meniscus in the burette in which the pressure of the gas has been adjusted by connecting through a manometer to a "compensator." In order that the gas in the compensator and burette may be under similar thermal conditions, the compensator is usually of the same shape and size as the burette and stands beside it in a water jacket. Unless the gas is dried before each measurement, a rare procedure, a part of its pressure is exerted by water vapor. To make this pressure definite and to automatically correct for it, a little liquid water is kept in the burette and compensator to insure a saturation pressure of water vapor in both. Under these conditions each unit volume of the burette will contain the same fraction of a mole of gas, excepting water vapor, throughout the analysis, and the volumes measured may be added to or subtracted from each other without correction.

Burettes for special purposes are frequently used for the analyses of gases the percentage composition of which varies but slightly from some normal condition. Such burettes ordinarily consist of one or more bulbs of relatively large diameter connected by graduated tubing of small diameter, so proportioned that the significant measurements are always read in one of the small calibrated tubes.

In the apparatus used by Carpenter[1] for the analysis of air the burette and compensator each consists of two large bulbs connected by three lengths of capillary tubing 2 mm in diameter. The vertical distance between the calibration marks permits readings of 0.001 percent of the burette volume to be made with reasonable precision. A corresponding precision with a cylindrical burette would be only 0.02 percent of the volume.

Recently the author undertook a series of analyses of outdoor air by means of the Carpenter apparatus. Some of the results were discouraging, and the possibility that the rate of saturation of the compensator was insufficient seemed the most probable explanation. It is customary to put water into the compensator of this apparatus but once during the life of the apparatus unless accidents occur or the water becomes dirty after several years of use. This water collects in the bottom of the compensator, and water vapor from this source must pass through 48 cm of capillary tubing in order to reach the upper bulb of the compensator. The manipulation of the apparatus requires the frequent admission of laboratory air, which may be relatively dry, to the top of the compensator, and the gas confined in this part is in contact through capillary connections with a 20-percent solution of potassium hydroxide which serves as the manometric fluid.

In the course of an analysis some transfer of gas back and forth between the compensator and manometer is unavoidable. The admission of laboratory air and the mild desiccating action of the potassium hydroxide solution may be expected gradually to exhaust the film of visible water on the compensator walls until only an adsorbed film of water is available to saturate the gas in the compensator. The thickness of this film will not necessarily be uniform and will depend on the recent history of the apparatus. One part of the film may be in equilibrium with the water vapor from the bottom of the compensator, while another part may be in equilibrium with the water vapor from the potassium hydroxide or the partial pressure of the laboratory air last admitted to the compensator.

II. EVAPORATION FROM GLASS SURFACES

The vapor pressure of films of water adsorbed on glass has been measured by McHaffie and Lenher.[2] According to these authors, the vapor pressure of the film is a function of its thickness. Their data indicate that there should be a significant difference between the vapor pressure of the visible film in the burette and the adsorbed film in the compensator whenever the latter film is less than several hundred molecules thick.

If a cylindrical compensator, 1 cm in diameter, is saturated at 19° C, approximately 60 molecular layers of water must evaporate from its walls to saturate the gas in it at 20° C. Within certain temperature limits, depending upon the history of the apparatus, sufficient water will evaporate from the film on the compensator walls to saturate the gas in the compensator. Above this limit water vapor must travel up the tube from the lower reservoir if the gas is to become saturated.

[1] Thorne M. Carpenter, J. Metabolic Research **4**, 1–25 (1923).
[2] I. R. McHaffie and S. Lenher, J. Chem. Soc. **127**, 1559 (1925).

III. CONVECTION

The movement of water vapor in tubes of very small internal diameter is chiefly by diffusion. Tubes of 6 and 9 mm diameter were used by different observers to determine the value of the diffusion constant of water vapor into air.[3] The data obtained by these investigators are in fair agreement and indicate that the effects of convection were small if present at all, under the conditions of their experiments.

Data on the conduction of heat across air spaces may be pertinent to the discussion of the movement of water vapor in so far as density relations are involved in the two cases. Such data indicate that convection becomes increasingly important in the conduction of heat as the distance across the air space increases and that convection is negligible, if it occurs at all, when the distance across the space is less than 1 cm.[4]

As a supplement to the data presented in this paper, the times required for ammonia vapor to pass up vertical tubes of different diameters were measured. Glass tubes 57 cm long and 3.1, 3.8, 7.6, 8.8, 15.4, 19.0, and 24.3 mm in diameter were used. Strips of congo red paper (blue by treatment with HCl gas) were held in place by cotton plugs at the upper ends of the tubes. The lower ends were immersed simultaneously in a solution of ammonium hydroxide and the times required for sufficient ammonia to pass up the tubes and begin to change the color of the indicator were measured. The relative times (time in the largest tube being taken as the unit) as calculated from the average of seven experiments, in the order of the diameters given above, were 3.3, 3.3, 3.1, 2.9, 2.6, 2.0, and 1. In the individual experiments the relative times were much larger when concentrated solutions of ammonium hydroxide were used and approached unity with dilute solutions which indicates that the density gradient in the tubes as well as their diameters is a controlling factor in initiating convection currents.

IV. DIFFUSION

The rate of diffusion of water vapor into air partially saturated with water vapor may be calculated closely enough to permit a conclusion to be drawn as to the order of magnitude of the time required to reach any given degree of saturation in a cylindrical vessel. The general equation for diffusion (Int. Critical Tables V, 62)

$$\frac{\delta p}{\delta t} = D\frac{\delta^2 p}{\delta x^2}$$

was solved and expanded [5] into a form that can be applied to the diffusion of water vapor occurring in narrow cylindrical compensators. The calculations were made for tubes of various lengths, and the time required to reach a given degree of saturation was plotted against the

[3] A. Winkelmann, Ann. Physik **258**, 7 (1884).
M. Le Blanc and G. Wuppermann, Z. phys. Chem. **91**, 150 (1916).
[4] H. C. Dickinson and M. S. Van Dusen, Am. Soc. Refrigerating Engrs. J. **3**, (1916).
P. E. Palmer and E. R. Weaver, BS Tech. Pap. **18**, 35 (1924) T249.
White, Phys. Rev. **10**, 743 (1917).
R. B. Kennard, BS J. Research, **8**, 787 (1932) RP452.
[5] The author is indebted to C. S. Cragoe and C. Snow of this Bureau for the mathematical treatment of the diffusion data.

degree of saturation. The data are presented in figure 1. The calculations assumed that the compensators were saturated at 20° and the temperature was then changed to and held constant at 21°. Gravitational effects were neglected and uniform temperatures were assumed throughout the system. The difference between the average partial pressure in the tube, at time t, and the saturation pressure of water at 21° is the ordinate, and time is the abscissa. The data indicate that approximately 5 hours must elapse in order that the volume readings from an apparatus employing a 48-cm cylindrical compensator will be accurate within 0.01 mm of Hg or approximately

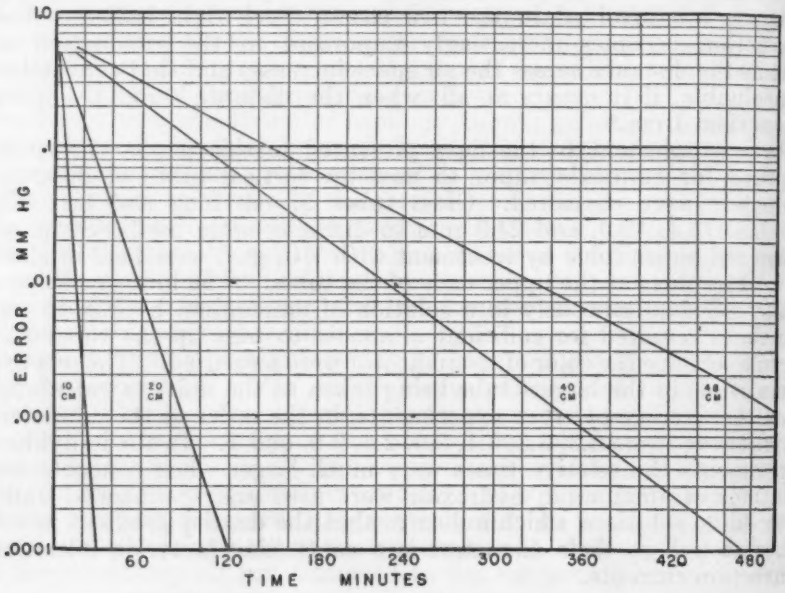


FIGURE 1.—*Calculated deficiency of saturation by diffusion after a 1° change of temperature.*

0.001 percent. When the compensator employed is of the bulb type and the bulbs comprise over 90 percent of the total volume, the time required to reach a given degree of saturation will be much longer than that indicated for cylindrical compensators. It is interesting to note that the time required to reach any given degree of saturation is proportional to the square of the length of the compensator, so that better compensation may be obtained by making this part of the apparatus shorter than the burette, even at the sacrifice of a certain degree of thermal similarity between the burette and compensator. The experimental data to be presented indicate that the same purpose may be accomplished by using a full-length compensator 1.5 cm or more in diameter.

V. APPARATUS AND PROCEDURE

The experimental data were obtained by means of apparatus A and B, shown in figure 2. The right side of A is similar to the compensator of the Carpenter apparatus. The right side of B is of the

same shape as the compensator of the gas-analysis apparatus used for general purposes. In the remainder of this paper the terms "burette" and "compensator" will be used to signify respectively the left and right sides of the apparatus. The diameter of the capillaries is 2 mm, and the diameter of the cylinder about 15 mm. Apparatus *B* was made by substituting the cylinder for the bulbed compensator after the data had been obtained from *A*. The left side of the apparatus, which was common to both *A* and *B*, was etched inside so that a film of liquid would be retained on the surface and its presence could be observed. The presence of this film at all times during the experiments corresponds to the condition which the analyst endeavors to maintain in a burette, and the pressure changes occurring in this side with changes of temperature may be regarded as similar to those occurring in a burette during an analysis.

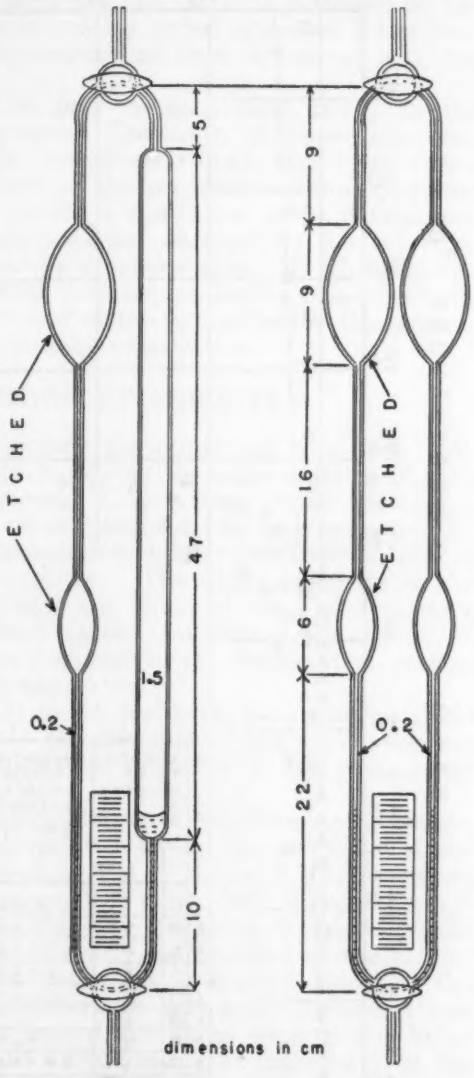
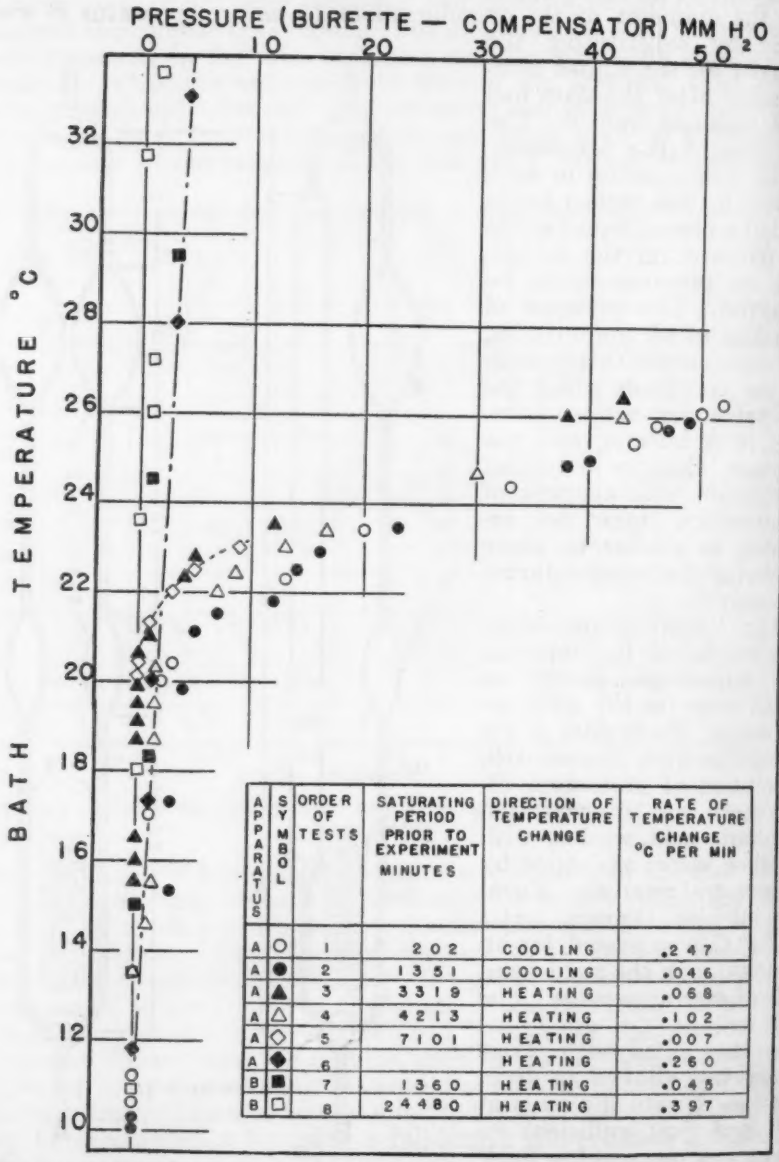


FIGURE 2.—*Apparatus used to measure the difference of pressure between the burette and compensators.*

The following procedure was employed in preparing the apparatus, except as noted later for the sixth experiment. Both sides of the apparatus were cleaned with a solution of potassium dichromate in concentrated sulphuric acid, washed with distilled water and dried by a current of room air. Room air bubbled through water at 24° C was passed for an hour through the right-hand side of each apparatus. The left side of the apparatus was then filled with water which was allowed to drain out slowly until the amount left was just sufficient to serve as a manometric fluid. The stopcocks were then turned to connect the burette and compensator of the apparatus, and part of the water in the burette ran into the lower part of the compensator and served as a manometric fluid and as a saturating reservoir. The upper stopcock was then closed and the apparatus

completely immersed in a vigorously stirred water bath. In addition to the stirring, the apparatus was rotated by hand about its vertical axis before observations were made, in order to obtain



APPARATUS	SYMBOL	ORDER OF TESTS	SATURATING PERIOD PRIOR TO EXPERIMENT MINUTES	DIRECTION OF TEMPERATURE CHANGE	RATE OF TEMPERATURE CHANGE °C PER MIN
A	○	1	202	COOLING	.247
A	●	2	1351	COOLING	.046
A	▲	3	3319	HEATING	.068
A	△	4	4213	HEATING	.102
A	◇	5	7101	HEATING	.007
A	◆	6		HEATING	.260
B	■	7	1360	HEATING	.045
B	□	8	24480	HEATING	.397

FIGURE 3.—*Effect of change of temperature on the difference of pressure between the burette and the compensators.*

similar thermal conditions in both sides. Rapid changes of temperature were accomplished by the addition of ice or warm water to the bath; gradual changes were accomplished by means of a copper U-tube immersed in the bath and connected to the hot- and cold-water supply.

VI. EXPERIMENTAL DATA

The experimental data are presented in figure 3. On this graph the temperature is plotted as the ordinate against the difference of pressure between the two sides of the apparatus as the abscissa.[6] The table at the bottom contains most of the data pertinent to the experimental procedure. The saturating period indicated is the total time that the gas in the compensator had been in contact with the manometric fluid.

The scattering of the points may be attributed chiefly to the behavior of the manometric system. The nature of the work necessitated the use of water as the manometric fluid, and there was a greased stopcock at the bottom of the manometer. The precision of the experiments does not permit a conclusion to be drawn concerning the exact degree of compensation obtained by the two compensators under the conditions of the experiments. The information obtained was a qualitative rather than a quantitative measure of the saturation of the compensators and of the role played in this process by diffusion, convection, and surface evaporation.

VII. DISCUSSION OF RESULTS

Previous to the sixth experiment the apparatus was filled with water, which was allowed to drain leaving the inner surfaces of both sides of the apparatus visibly wet. Under these conditions only a slight difference of pressure existed between the two sides of the apparatus over the entire temperature range investigated, in spite of the very rapid change of temperature. The slight difference in the degree of saturation may indicate the effect of the etched surface or a small thermal difference between the two sides of the apparatus. There is no indication of a sharp change in the degree of saturation reached in the two sides of the apparatus.

The first five experiments, *A*1 to *A*5, inclusive, were made without altering the stopcocks and only the left side of the apparatus was visibly wet. The right side had been subjected to the preliminary treatment described in section V.

The plotted data from these five experiments indicate an increasing difference in the degree of saturation between the two sides of the apparatus at temperatures above 20.5° C. Below this temperature the compensation was about as good as when both sides of the apparatus were visibly wet. The break in the curve is sharp and the temperature at which it occurs is nearly independent of the rate of temperature change or of the period of saturation prior to the experiment. There is a slight difference between the observations when the apparatus was being heated and those when it was being cooled. This difference may be an indication of inaccuracy in the manometric system. It is evident that neither diffusion nor convection supplies water vapor to the compensator, above 20.5° C, at rates which are adequate to saturate it when the rate of change of temperature is 0.007° per minute.

[6] This method of presenting the data differs from a gas analysis determination in that the volume of the compensator is not constant but changes with the movement of the manometric fluid. If the volume of the compensator in the experimental apparatus had been kept constant, the pressure differences given in figure 3 would have been about 50 percent greater than those recorded.

The slope of the curves above 20.5° C in the first five experiments is determined by the amount of water vapor supplied to the compensator by evaporation from the walls, and by diffusion, and convection of water vapor from the water meniscus during the experiment. Within the limit of experimental error these slopes are the same and indicate that equal amounts of vapor were supplied in all five experiments. Since the saturating period per degree change of temperature (the reciprocal of the rate of temperature change) varied from 4 minutes in the first to 143 minutes in the fifth experiment and did not measurably affect the amount of vapor supplied, the effects of convection and diffusion must have been very small. In view of this fact the saturation attained when heating below 20.5° C must have been affected by the evaporation of the water on the walls of the compensator.

The experiments *B*7 and *B*8 were made with apparatus *B*, figure 2. The cylinder which replaced the bulbed compensator was subjected to the same preliminary treatment as the latter and presumably had a similar film of adsorbed water on its inner surface. The data indicate that reasonably accurate compensation was afforded by the cylindrical compensator at higher rates of change of temperature than will be encountered under normal laboratory conditions, and at temperatures above those at which the bulbed compensator may fail to give even approximately accurate results.

On the basis of the calculated rates of diffusion given in figure 1, the saturation of the cylindrical compensator resulted chiefly from convection. The rapid equalization of pressure in the two sides of apparatus *B*, as shown by the movement of the manometric fluid when this apparatus was subjected to sudden increases of temperature, and by the absence of a similar movement under like conditions with apparatus *A*, also indicates that convection was chiefly responsible for the saturation of apparatus *B* at the higher temperatures. The data on the movement of ammonia in tubes of different diameters also indicate that the effects of convection will be greater in the wide cylindrical compensator.

The accuracy of volumetric measurements in a gas-analysis apparatus will be a function of the time required to saturate the compensator as compared with the saturation period of the burette. The presence of water on the walls of the burette ensures rapid saturation at all times and the accuracy of the apparatus, insofar as saturation is involved, will depend on the time required to saturate the compensator and the rate at which the temperature of the apparatus is increasing.

The degree of saturation of a "dry-walled" compensator must necessarily lag behind that of a "wet-walled" burette when the temperature of the apparatus is increasing, and the difference in saturation will be a function of the rate of temperature change as well as the shape of the compensator. This difference in saturation may be made small by eliminating any features in the design of the compensator which hinder the free movement of water vapor, but cannot be eliminated entirely if the distance that water vapor must travel is different in the two vessels being saturated.

CONCLUSION

In order to obtain a similar rate of transfer of heat from a water jacket through the walls of the burette and compensator of a gas-analysis apparatus, these parts are made of the same material and are of the same shape and size, but unavoidably are not of the same thickness. The benefits in volumetric accuracy resulting from this thermal similarity must be very small because the burette and compensator stand close together in a water jacket and the position of the mercury in the burette may be anywhere between the top and bottom of the water jacket, while the entire length of the compensator is always gas-filled.

To maintain a saturated condition of the gas, the water in a compensator of the type used by Carpenter is confined in the bottom of a tube of 2 mm diameter, and visible water on the walls above this tube is avoided because it tends to run down and plug the narrow tubes joining the compensator bulbs.

The data indicate that the rate of travel of water vapor upward from the bottom of a capillary 2 mm in diameter is too slow to appreciably affect the degree of saturation of a gas confined in the body of a bulbed compensator. If there is no visible water on the walls of such a compensator, the only source of water vapor, for saturation purposes, is the film of adsorbed water on the glass walls. The thickness of this film and its vapor pressure will depend on the temperature of the compensator and the amount of water vapor in the gas in the compensator. Above some limiting temperature, corresponding to the break in the curve of figure 3, which will depend on the volume and humidity of the laboratory air admitted to the compensator, the manipulation of the apparatus and the vapor pressure of the potassium hydroxide solution in the manometer, the gas in the compensator will not be saturated; and serious volumetric errors will occur in an analysis whenever the temperature of the apparatus changes in either direction. At temperatures which are lower than the temperature which is critical for the particular conditions and apparatus, the error of compensation will be small and will depend on the relative rates of heat transfer to the burette and compensator rather than on the travel of water vapor. The data of figure 3 indicate that errors resulting from incomplete saturation in the compensator may be largely avoided by using a relatively wide cylinder as a compensator. This, of course, will result in the sacrifice of whatever benefits there may be in the thermal similarity of the burette and compensator. One method to retain partial thermal similarity, and at the same time insure more rapid saturation of the gas in the bulbs of the compensator, would be to extend the capillary tubes up into the body of each of the bulbs, so that the walls of the bulbs could be visibly wet without danger of the water in them draining into the capillaries to form slugs.

WASHINGTON, September 4, 1936.

U. S. Department of Commerce National Bureau of Standrads

RESEARCH PAPER RP963

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

LABORATORY CORROSION TESTS OF WELDED LOW-CARBON STAINLESS STEEL

By George A. Ellinger and Leon C. Bibber *

ABSTRACT

Welded specimens of low-carbon stainless steel (less than 0.06 percent of carbon) were exposed to the corrosion attack of three different solutions. Results of these tests were as follows:

In a copper sulphate-sulphuric acid solution, intergranular corrosion did not occur in either plate or weld metal regardless of the heat treatment.

In boiling nitric acid, intergranular corrosion occurred only in certain heat-treated plates of low-carbon stainless steel. Intergranular corrosion did not occur in welded metal, with or without heat treatment.

In hydrochloric acid of high concentration, the corrosion rate of plate metal was not affected by heat treatment, but the corrosion rate of weld metal was considerably decreased by heat treatment at high temperatures. Intergranular corrosion was not observed in any specimen exposed to this reagent.

These results can be explained on the basis of selective attack by the corrosive agents on certain constituents of the steel samples.

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I. INTRODUCTION

The incorporation of laboratory corrosion tests into specifications for stainless steels has caused considerable controversy regarding the interpretations of results of such tests.

Three types of corrosion are usually recognized, (1) general, which is a simple chemical reaction over most of the surface; (2) pitting, depending upon surface conditions found in localized areas and bearing no relation to structural features; and (3) intergranular, i. e.; localized corrosion progressing along grain boundaries.

The unsatisfactory behavior in service of supposedly corrosion-resistant alloys has been traced in part to intergranular corrosion that is associated with chromium-rich carbides localized in or at the grain boundaries. It is well established that heating within the temperature range of 550° to 800° C ("sensitization") accelerates the formation

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of these carbides and hence increases the susceptibility to intergranular attack. During welding, certain portions of the metal adjacent to the weld are heated to within this range. Consequently, a welding test is frequently used to determine the susceptibility of material to carbide precipitation and intergranular corrosion.

Several laboratory corrosion methods have been recommended for testing materials that have been sensitized. It has been claimed that the results of these tests are a combination of intergranular, pitting and general corrosion and that no one of them is entirely reliable.

The investigation here reported was a study of these laboratory tests to determine their reliability for indicating susceptibility to intergranular corrosion of welded low-carbon 18–8 steel.

II. MATERIAL

The material from which the welded specimens were prepared was ⅜-inch (1 cm) plate of a low-carbon corrosion-resisting steel of the 18–8 type, purchased by the United States Navy Department for general welding tests. Arc welds were made with coated welding rods of about the same composition.

The chemical compositions of the plate, welding rod and deposited weld metal are given in table 1, and the type composition of the coating is given in table 2.

TABLE 1.—*Chemical composition of plate, welding rod, and deposited weld metal*[1]

Elements	Plate	Welding rod	Weld metal
	%	%	%
Carbon	0.054	0.06	0.06
Manganese	.40	.52	.50
Phosphorus	.025	.029	.031
Sulphur	.016	.007	.005
Silicon	.30	.34	.14
Chromium	18.59	19.26	18.86
Nickel	9.30	9.07	9.09
Copper	.01	.01	.01
Titanium	nil	nil	nil
Vanadium	.045	.04	.03
Molybdenum	nil	nil	nil
Selenium	nil	nil	nil
Nitrogen	.033	.032	.054

[1] Analyses made by Chemical Laboratory, Philadelphia Navy Yard, Philadelphia, Pa.

TABLE 2.—*Proximate analysis*[1] *of the coating on the welding rod*

Loss at 105° C	2.6%
Calcium fluoride	43.5%
Calcium oxide in excess of calcium present as calcium fluoride	8.2%
Magnesium oxide	3.6%
Aluminum oxide	5.8%
Ferric oxide	1.2%
Manganese oxide	0.5%
Sodium oxide	Present
Carbon dioxide	16.5%
Silica	12.1%
Manganese dioxide	2.6%
Total	99.6%

[1] Made by Chemical Laboratory, Philadelphia Navy Yard, Philadelphia, Pa.

Specimens consisting entirely of weld metal were prepared by building up alternate layers of longitudinal and transverse beads on a portion of a plate, as shown in figure 1. On one plate the welding was done continuously, with pauses long enough between beads to permit cleaning off of the slag; on another plate the material was quenched

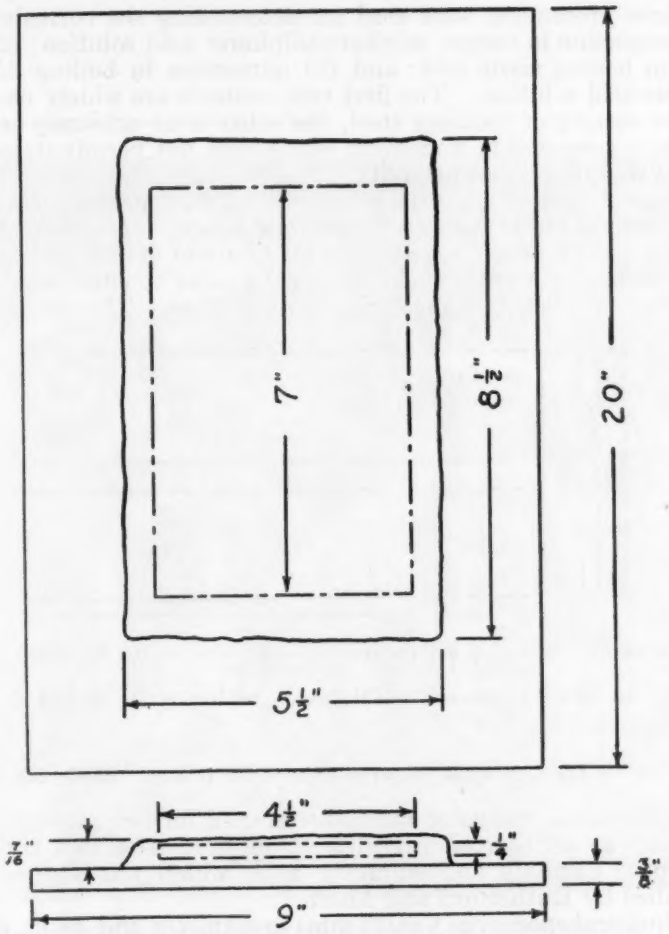

FIGURE 1.—*Method of building up solid layers of weld metal*

Specimens were taken from the areas within the dotted lines.

in water after each bead was laid and before the slag was cleaned off. The plates were not preheated prior to welding.

Single V-butt welds were made between two sections of plate, as shown in figure 2. The welds were laid in four longitudinal beads. The initial bead at the bottom of the V was retained by means of a backing strap of the same material as the plate. Two pairs of plates were welded in this manner, one of which was quenched after the deposition of each bead, and the other was welded continuously. Specimens containing the welded joint were machined from each pair of plates.

Throughout the work, a coated welding rod 5/16 in. (5 mm) in diameter was used as the positive electrode and the plate as the negative, with a direct-current arc operated at 23 volts and 170 amperes.

III. CORROSION TESTS

Three procedures were used for determining the corrosive attack: (1) immersion in copper sulphate-sulphuric acid solution; (2) immersion in boiling nitric acid; and (3) immersion in boiling 6*N* hydrochloric acid solution. The first two methods are widely used in corrosion testing of stainless steel, the other is an arbitrary method to measure corrosion in a medium which does not permit stainless steel to develop its normal passivity.

In order to determine the effect of heat treatment on the corrosion resistance, some of the specimens were heated for 1 hour at 980° C. and air cooled, others were heated for 1 hour at 650° C and air cooled; the remainder were left in the "as welded" condition. All heat treating was done in an electric muffle furnace. The specimens were

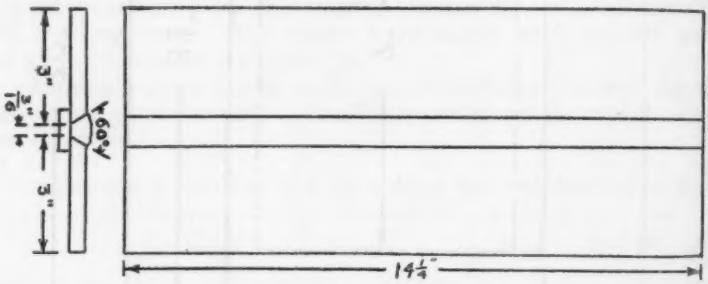

FIGURE 2.—*Method of making single V-butt welds joining two plates together.*

packed in sand in small metal boxes which were sealed to prevent oxidation.

1. TESTS IN COPPER SULPHATE-SULPHURIC ACID SOLUTION

An electrical resistance method was used for indicating the extent of intergranular corrosion resulting from immersion in a hot solution of copper sulphate and sulphuric acid, which was similar to that described by Rutherford and Aborn.[1]

Cylindrical specimens 1/8 in. (3 mm) in diameter and 4½ in. (11.4 cm) long were used. On specimens of the plate or weld metal, gage marks 1½ in. (3.8 cm) apart were made with a prick punch. On the welded-joint specimens, four gage marks, *A*, *B*, *C*, and *D*, were laid off at ½ in. (1.3 cm) intervals (fig. 3). The two inside marks, *B*, and *C*, were located in the plate adjacent to the weld, that is, between the weld and the zone of pronounced carbide formation. The resistance measured between points *B* and *C* was the combined resistance of the weld metal and bond zones. Measurements between *A* and *B* and between *C* and *D* gave information on the resistance of the two zones that were rich in carbides. Measurements between *A* and *D* were also made.

[1] Trans. Am. Inst. Min. Met. Eng. **100**, 293 (1932).

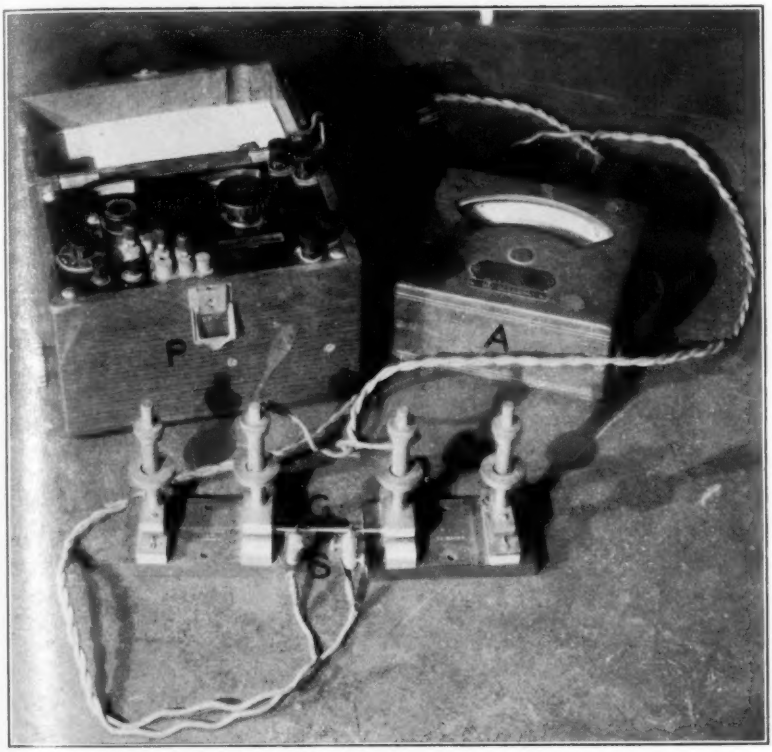

FIGURE 4.—*Apparatus for measuring resistance of specimens used in copper sulphate-sulphuric acid corrosion tests.*

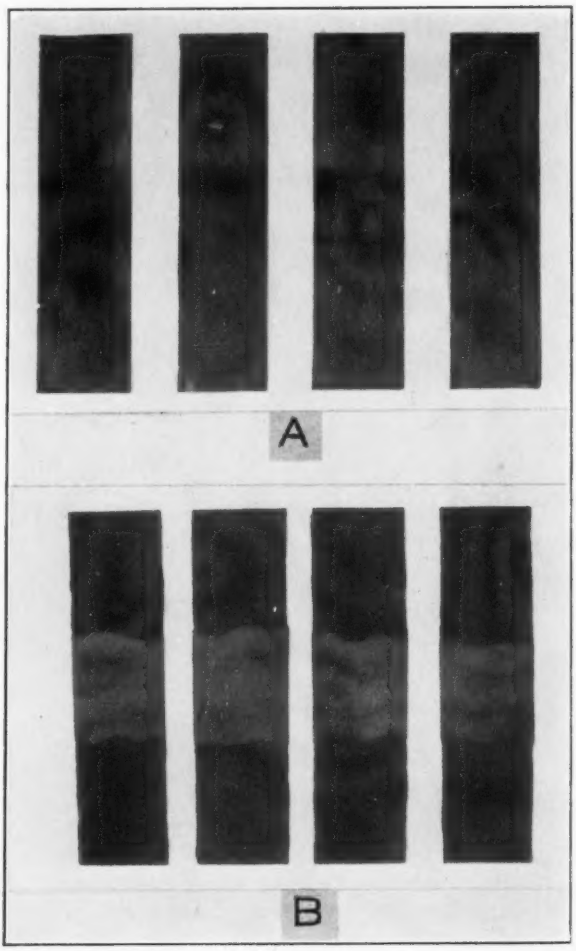

FIGURE 8.—*Specimens containing a single* V*-butt joint after corrosion in boiling nitric acid.*

A. No heat treatment after weld was made.
B. Heat treated at 650° C for 1 hour.

In using the apparatus, shown in figure 4, for measuring the resistance of the specimens in their initial condition and after corrosion, the copper contact points, *C*, were centered in the gage marks of the specimen *S*. The direct current, measured with the ammeter *A*, was maintained at 5 amperes. The voltage drop across the points was measured with the potentiometer *P*. The resistance was calculated from the values obtained.

The corrosion apparatus consisted essentially of a 1-liter erlenmeyer flask fitted with a reflux condenser. Four test specimens, and one sensitized control specimen that contained 0.10 percent of carbon, were immersed, after initial resistance measurements, in 500 ml of the corroding solution, consisting of 13 g/liter of $CuSO_4.5H_2O$ and 47 ml/liter of H_2SO_4 (sp gr 1.84). The solution was maintained at the boiling point for 24 hours. The electrical resistance of each specimen was again determined. The specimens were then treated in a fresh portion of solution for an additional 76 hours, after which the resistance was again determined.

The changes in electrical resistance as a result of exposure to the copper sulphate-sulphuric acid solution were small, that is from −4.6 to +7.7 percent, and showed no definite trend, regardless of heat treatment or time of exposure. (The sensitized control specimens, which had a higher carbon content, had an increase in resistance of slightly more than 100 per cent.) All test specimens that had been heat treated for 1 hour at 650° C were reheated at the same temperature for 23 additional hours. These were exposed to the boiling copper sulphate-sulphuric acid solution for 100 hours. The resistances of these specimens were of the same order as of those heat treated for only 1 hour, and indicated that no intergranular corrosion had taken place.

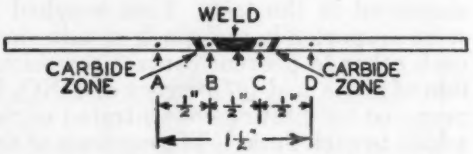

FIGURE 3.—*Specimens for copper sulphate-sulphuric acid corrosion, showing location of reference marks.*

These results agree with those of Rutherford and Aborn for steels containing less than 0.06 percent of carbon, but are in marked contrast with their results for steels containing 0.07 to 0.20 percent of carbon, in which several hundred percent increase in electrical resistance accompanied intergranular corrosion. However, the results of corrosion of the control specimens were quite similar to those of Rutherford and Aborn for similar high-carbon material.

Because the changes in resistance were so small, it seemed probable that no appreciable intergranular corrosion had occurred. Cross sections of ends of the tested specimens were polished and examined under the microscope. Numerous carbides were found at the grain boundaries but no traces of corrosion were detected, even in the specimens of plate metal that had been heat treated for prolonged periods at 650° C.

From these experiments it was concluded that exposure to the copper sulphate-sulphuric acid reagent does not cause intergranular corrosion in this low-carbon material, even after prolonged heat treatment to intensify the formation of carbides. However, the re-

agent does cause intergranular attack in stainless steel of higher carbon content, as noted in the results of corrosion of the sensitized control specimens containing 0.10 percent of carbon.

Bain, Aborn, and Rutherford [2] concluded that the copper sulphate-sulphuric acid reagent attacked only those portions of the grain, adjacent to the grain boundaries, that had been depleted in chromium as a result of the formation of carbides at the grain boundaries; and that the reagent did not attack the carbides themselves. The results of the present investigation are in agreement with this conclusion.

2. TESTS IN BOILING NITRIC ACID

The test in boiling nitric acid, described by Huey, [3] has been incorporated in many specifications to establish the resistance of stainless steels to corrosion under oxidizing conditions. The procedure was studied by subcommittee IV of committee A–10 of the American Society for Testing Materials with the conclusion [4] that the test is "capable of furnishing accurate, reproducible, quantitative data."

The apparatus used for corroding the specimens was the same as that used for the copper sulphate-sulphuric acid tests. Rectangular specimens, 1⅞ in. by ½ in. by ¼ in. (4.8 cm by 1.3 cm by 6 mm), were employed in the test. Four weighed specimens of a given material were supported in each flask on thin glass rods and were separated from each other to prevent contact corrosion. 500 ml of an aqueous solution of nitric acid (67 percent of HNO_3 by weight, with a sp gr of 1.408 prepared by diluting concentrated nitric acid with distilled water) was added to each flask. The contents of the flasks were maintained at the boiling point for 48 hours. The specimens were then removed, cleaned, dried, and weighed. The process was repeated until each set of specimens had been subjected to five 48-hour tests, 500 ml of fresh acid being used each time. The corrosion rate for each period was computed in inches penetration per month, from the loss of weight, surface area, density of material, and corrosion period (48 hours).

The results obtained from the immersion in boiling nitric acid are given in figures 5 to 7, inclusive. Each plotted point is the average of at least two observations, which were generally in excellent agreement.

Figure 5 shows the results obtained with the plate material. Specimens that were not heat treated showed a very low progressive rate of attack, which was almost identical with the attack of the material that had been heated for 1 hour at 980° C. Specimens heated at 650° C for 1 hour showed a very much greater rate of attack than other specimens, a sharp increase in rate being noted after the second 48-hour corrosion period. At the higher rates of attack, the lack of close agreement in the results obtained in duplicate runs is indicated by the shaded area of the curve.

The results obtained with weld metal specimens are given in figure 6. The effect of heat treatment in promoting the corrosive attack was insignificant. The rates of attack for all the specimens were very low and were similar to the rates for plate metal in the "as rolled" condition or after heat treatment at 980° C. Specimens which had been

[2] Trans. Am. Soc. Steel Treating **21**, 481 (1933).
[3] Trans. Am. Soc. Steel Treating **18**, 1126 (1930).
[4] Proc. Am. Soc. Testing. Materials **33**, I, 178 (1933).

heated at 650° C corroded at substantially the same rates as those heated at 980° C.

In figure 7 are summarized the results obtained with specimens of the plate containing a welded joint. The corrosion rates were quite similar to those of the plate, probably because the greater portion of each of these specimens was plate metal.

The extent of attack by the boiling nitric acid could be roughly estimated from the appearance of the corroded specimens. The entire

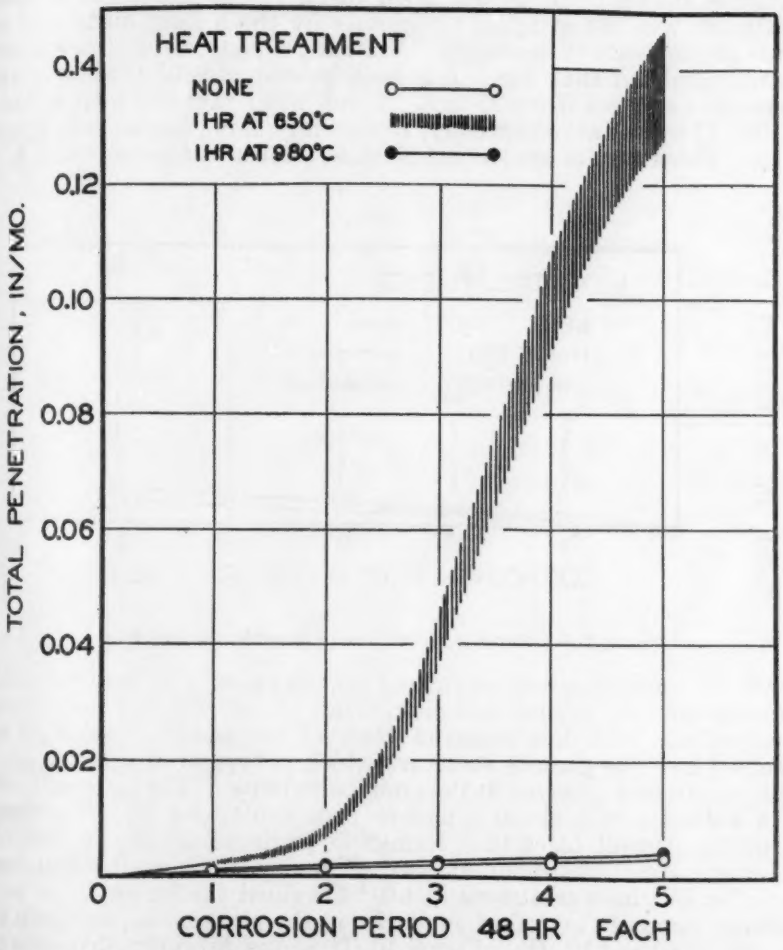

FIGURE 5.—*Corrosion of plate metal in boiling nitric acid.*

surface of each specimen was uniformly affected. The surfaces of specimens which were attacked slowly (see fig. 5 and 6) were only slightly etched. The surfaces of the specimens that had been heat treated at 650° C, were roughened to a much greater extent. These effects were particularly noticeable in the specimens containing both weld and base metals. As shown in figure 8, the corrosion of "as welded" specimens was relatively slight and quite uniform over the entire surface. The appearance of the specimens that had been heat

treated at 980° C was quite similar to that of the "as welded" specimens. On the other hand, in the specimens which had been heat treated at 650° C, the plate was severely roughened, the weld metal being left in bold relief.

The specimens of plate and weld metals that had been tested in the copper sulphate-sulphuric acid solution and that showed no attack by this reagent were placed in boiling nitric acid and their resistances were measured after each of three 48-hour periods. The results of these tests are shown in figure 9. Weld metal in any condition of heat treatment was not attacked sufficiently by the boiling nitric acid to cause any increase in resistance. Neither the plate metal that was not heat treated nor that which was heat treated at 980° C showed appreciable increases in resistance. Plate metal that was heat treated at 650° C was attacked severely, as shown by large increases in resistance. These results are similar to those shown in figures 5 and 6.

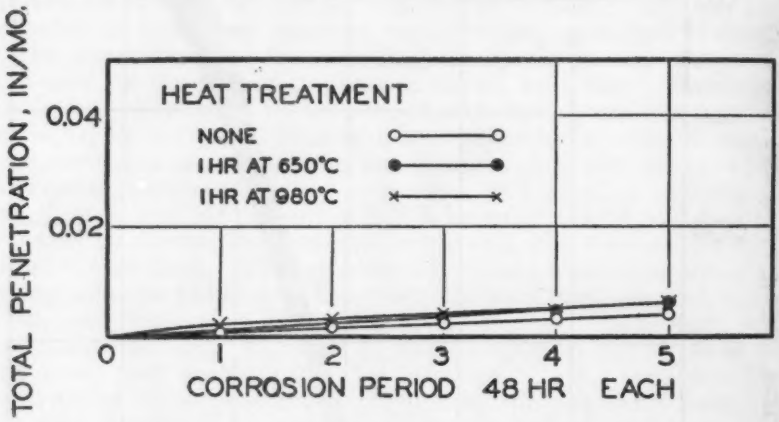

FIGURE 6.—*Corrosion of weld metal in boiling nitric acid.*

All the specimens were examined microscopically to determine the structure and the amount and distribution of carbides, and to correlate these effects with the observed rates of corrosion.[5] The plate as received had the gamma structure which is typical of this material, with no carbides localized at the grain boundaries. The plate adjacent to a welded joint showed a narrow zone containing grain-boundary carbides, a result of carbide formation produced by heating during welding. Heat treatment at 980° C removed all evidence of free carbides, but heat treatment at 650° C caused the formation of carbides at some of the grain boundaries in the plate metal, as shown in figures 10 (*C*) and 10 (*D*). Figure 10 (*D*) shows, however, that some of the grain boundaries were free from carbides.

Examination of specimens of the weld metal, built up either by intermittent or by continuous deposition, revealed interesting differences in structure (fig. 10(*A*) and (*B*)). After heat treatment at 650° C, both metals consisted of a matrix of gamma iron with numerous small areas of delta ferrite, each of the latter being outlined by carbides. In the intermittently deposited metal (fig. 10(*A*)) the

[5] The etchant used for revealing carbides and grain boundaries was 10-percent oxalic acid, the use of which is described in Trans. Am. Soc. Metals **24**, 26 (1936); also Etching Stainless Steels, NBS Technical News Bul. 218, p. 62 (June 1935).

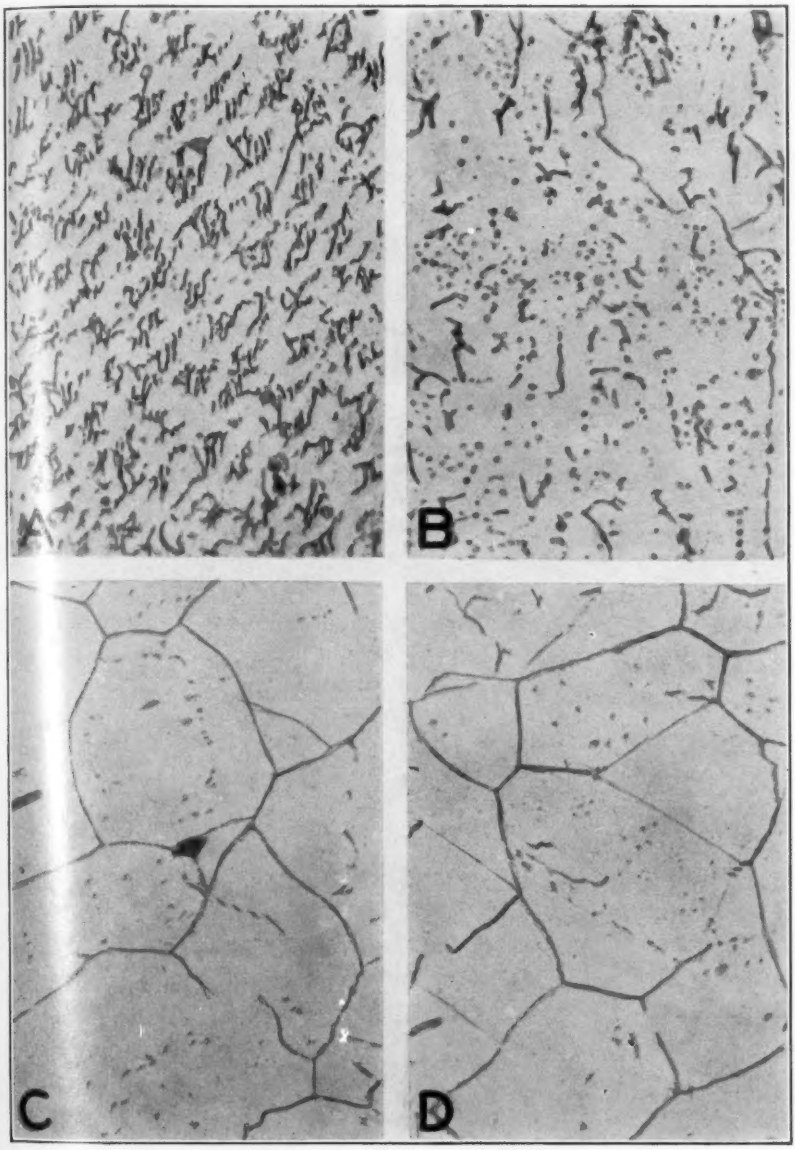

FIGURE 10.—*Structures of specimens treated at 650° C for 1 hour.*

Etched electrolytically in 10-percent oxalic acid. Magnification, 500×.
A. Weld metal, quenched between beads.
B. Weld metal, deposited continuously.
C. Plate metal, etched for carbides only.
D. Plate metal, etched for carbides and grain boundaries.

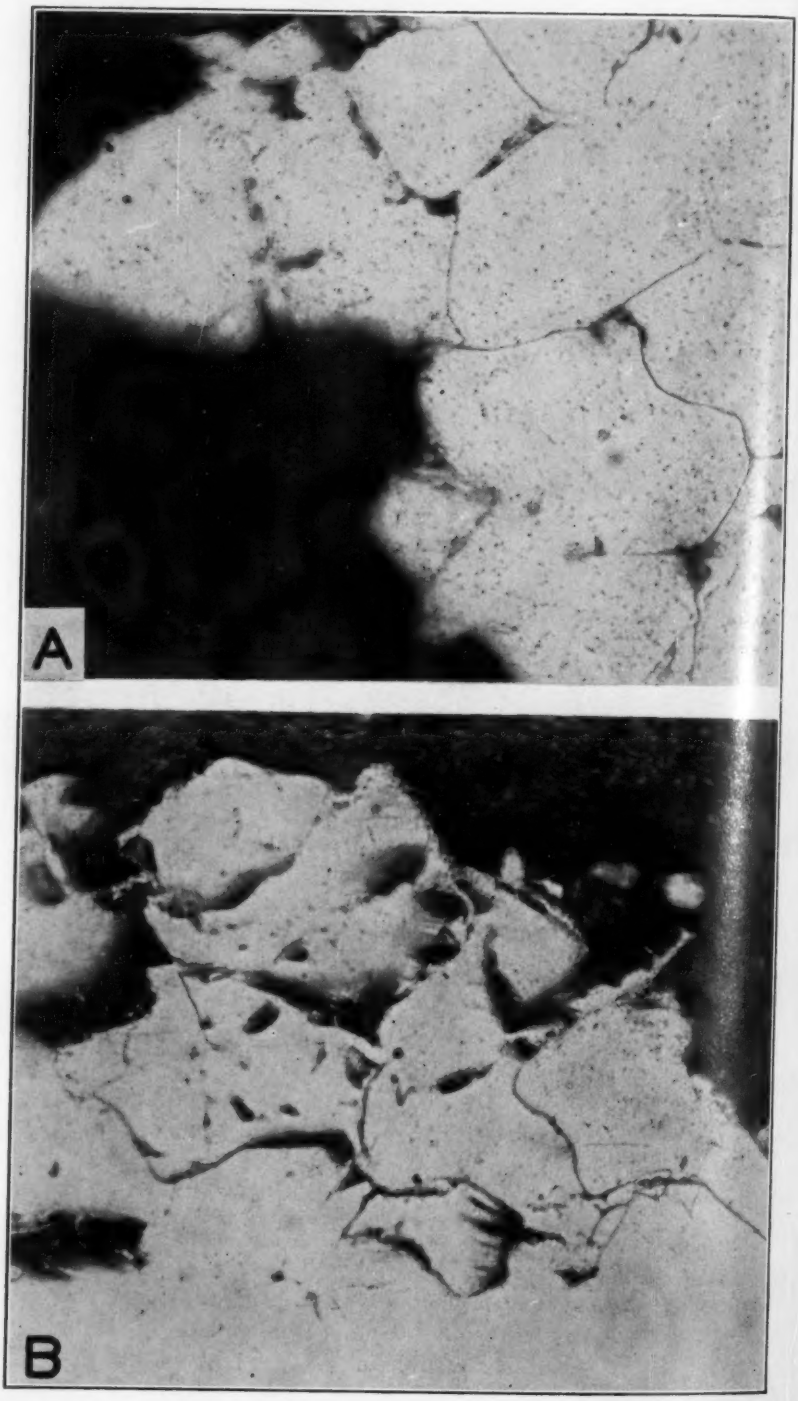

FIGURE 11.—*Edges of a specimen of plate metal, heat-treated at 650° C and corroded in boiling nitric acid.*

Specimen not etched after corrosion. Magnification, 500×.

areas of delta ferrite were elongated and so narrow that the outlining carbides appear to be short lines or dendrites. In the continuously deposited metal (fig. 10(*B*)) the areas of delta ferrite were larger and were frequently circular in outline. There was no evidence of carbide formation in the gamma areas and it is noteworthy that the carbides did not concentrate at the grain boundaries of the weld metal as they did in the plate metal.

All the specimens that had been corroded in boiling nitric acid showed evidence of nonselective corrosion, but intergranular corrosion

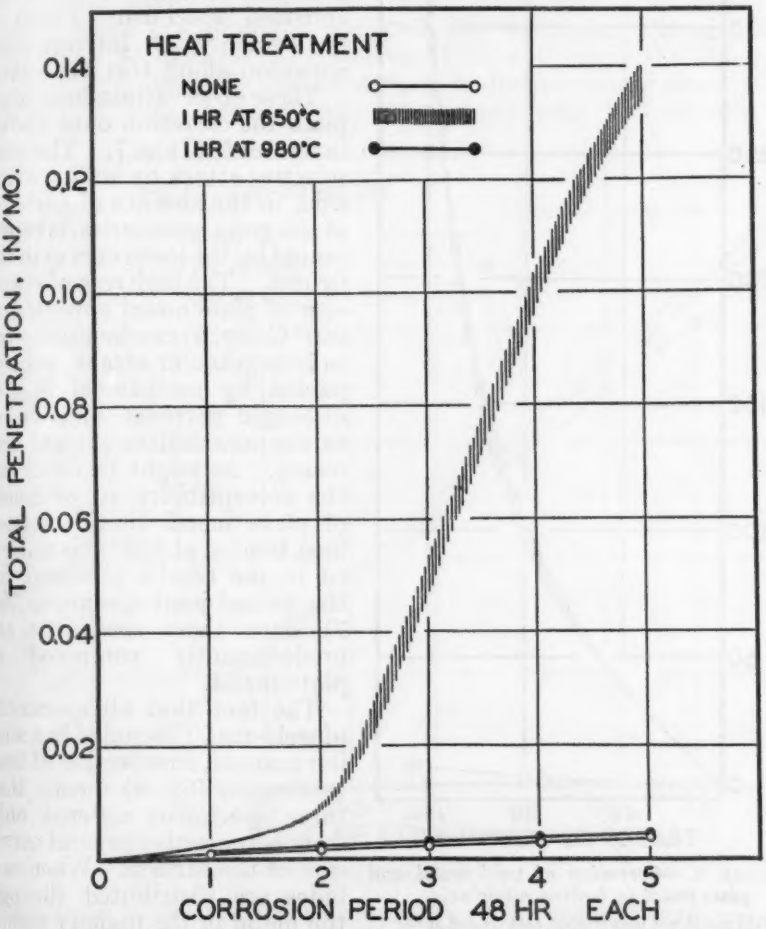

FIGURE 7.—*Corrosion of welded specimens in boiling nitric acid.*

was found only in those specimens that had been heat treated at 650° C. Figure 11 shows that in some cases intergranular corrosion progressed to such an extent that grains were completely separated or even dislodged. Further evidence of loosening of the grains through intergranular corrosion was obtained in the fourth and fifth corrosion periods of plate specimens annealed at 650° C, when a gray powder collected on the bottom of the corrosion flask. This powder, found only with plate specimens annealed at 650° C, con-

sisted of grains of metal that were evidently detached from the specimens; carbide particles were not detected.

Figure 12 shows a corroded specimen, similar to that of figure 11, after etching with oxalic acid to reveal free carbides and grain boundaries. It is evident that intergranular corrosion occurred only along those grain boundaries where carbide had been formed. In the upper right corner of figure 12(*B*) a carbide-free boundary can be identified, extending vertically to the outer edge of the corroded specimen. There is no evidence of intergranular corrosion along this boundary.

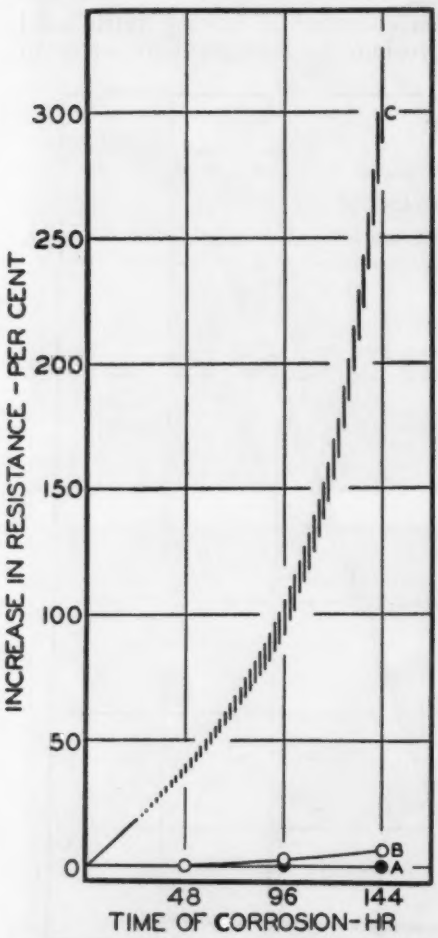

FIGURE 9.—*Corrosion of weld metal and plate metal in boiling nitric acid.*

A. Weld metal, not heat treated, heat treated at 650° C, and at 980° C.
B. Plate metal, not heat treated, and heat treated at 980° C.
C. Plate metal, heat treated for 24 hours at 650° C.

These observations help to explain the corrosion data shown in figures 5, 6, and 7. The nonselective attack by boiling nitric acid, in the absence of carbides at the grain boundaries, is represented by the lower curves in the figures. The high rate of corrosion of plate metal annealed at 650° C (fig. 5) can be attributed to intergranular attack, accompanied by mechanical loss of dislodged particles, in addition to the nonselective general corrosion. As might be expected, the susceptibility to corrosion of plate metal that has been heat treated at 650° C is reflected in the results obtained for the welded-joint specimens (fig. 7) since these specimens are predominantly composed of plate metal.

The fact that all specimens of weld-metal corroded in a similar manner, irrespective of heat treatment, (fig. 6) means that these specimens suffered only from nonselective general corrosion of the surface. When carbides are distributed through the metal in the manner shown in figures 10(*A*) and 10(*B*), they are not conducive to intergranular attack by nitric acid.

The attack of boiling nitric acid on low-carbon stainless steels is therefore twofold in nature, and involves a nonselective general corrosion of all exposed surfaces and a selective intergranular attack along grain boundaries where carbides are localized. The intergranular corrosion results in loss of loosened grains and, for this

type of steel, is much more destructive than is corrosion of the general type. Since it is known that boiling nitric acid decomposes chromium carbides, it may be assumed that the intergranular attack in these specimens proceeds by the destruction of the carbides in the grain boundaries.

3. TESTS IN HYDROCHLORIC ACID

The opinion is generally held that stainless steels owe their corrosion resistance to the tendency of chromium to form a protective film under oxidizing conditions. Since nitric acid is an active oxidizing agent and probably promotes film formation, the nitric acid test sheds no light on the corrosion of these alloys in the absence of a protective film. On the other hand, hydrochloric acid destroys this protective film. Consequently, some tests with hydrochloric acid

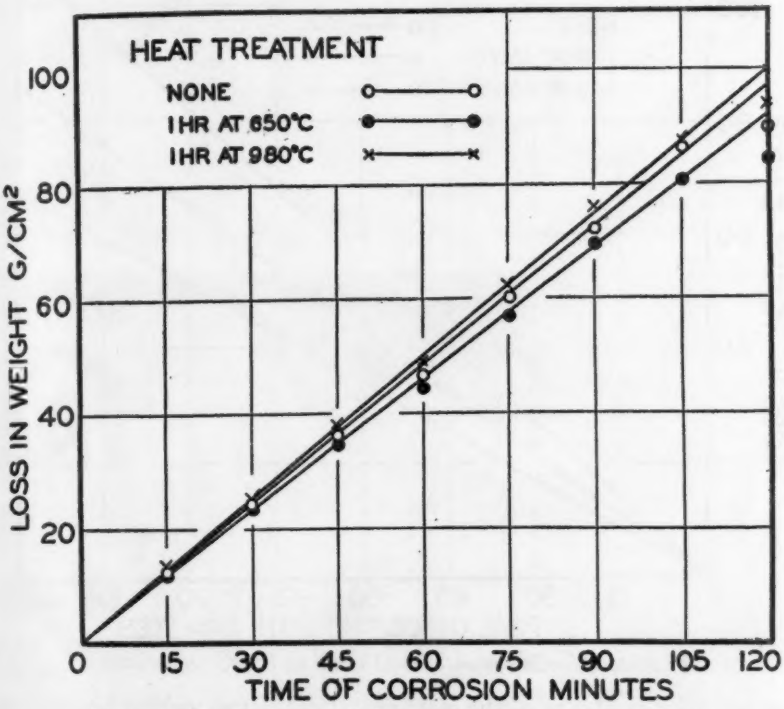

FIGURE 13.—*Corrosion of plate metal in hydrochloric acid.*

were made to observe the susceptibility of the specimens to corrosion in the absence of a protective film.

300 ml of a solution consisting of equal volumes of distilled water and concentrated hydrochloric acid (1.18 sp gr), was used in a covered beaker of 600 ml capacity. Two specimens similar to those used for the nitric acid tests were immersed for 15 minutes in the boiling solution. The specimens were cleaned, dried, and weighed before and after each 15-minute immersion. Eight 15-minute periods constituted a test run, the solution being replaced with a fresh one at the end of the fourth period. Results of these tests, calculated as loss

of weight in g/cm², are shown in figures 13 to 15, inclusive. Each plate specimen lost weight at approximately a constant rate throughout the duration of a test. Furthermore, as shown in figure 13, the rate of corrosion of a plate metal specimen was not appreciably affected by heat treatment at either 650 or 980° C. Specimens of weld metal that were not heat treated lost weight continuously and at about the same rate as did the plate metal. However, as shown in figure 14, heat treatment of the weld metal had a measurable effect on the rate of corrosion. Heat treatment at 650° C decreased the susceptibility of weld metal to attack, and heat treatment at 980° C decreased it further. In the latter condition the loss of weight of the weld metal was definitely less than that of the plate. The greater

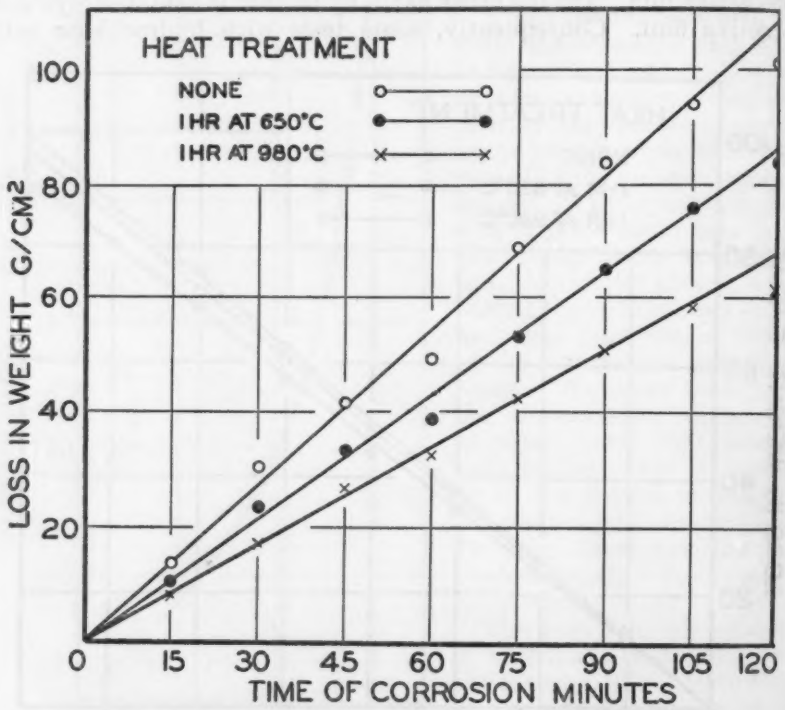

FIGURE 14.—*Corrosion of weld metal in hydrochloric acid.*

susceptibility to attack of the weld metal in the "as welded" condition, presumably accounts for the greater loss in weight of some of the welded joints (fig. 15).

There is no satisfactory explanation for these differences between weld metal and plate, or for the effect of heat treatment of the weld metal.

There was no evidence of selective attack at the grain boundaries. On the other hand, selective attack of the pitting type occurred on the surface of all specimens, particularly of the weld metal. In welded specimens without heat treatment the weld metal corroded at a faster rate than the plate, as is shown in figure 16 (*A*). However, after heat treatment of the welded joints at either 650 or 980° C, the weld metal was slightly more resistant than the plate metal.

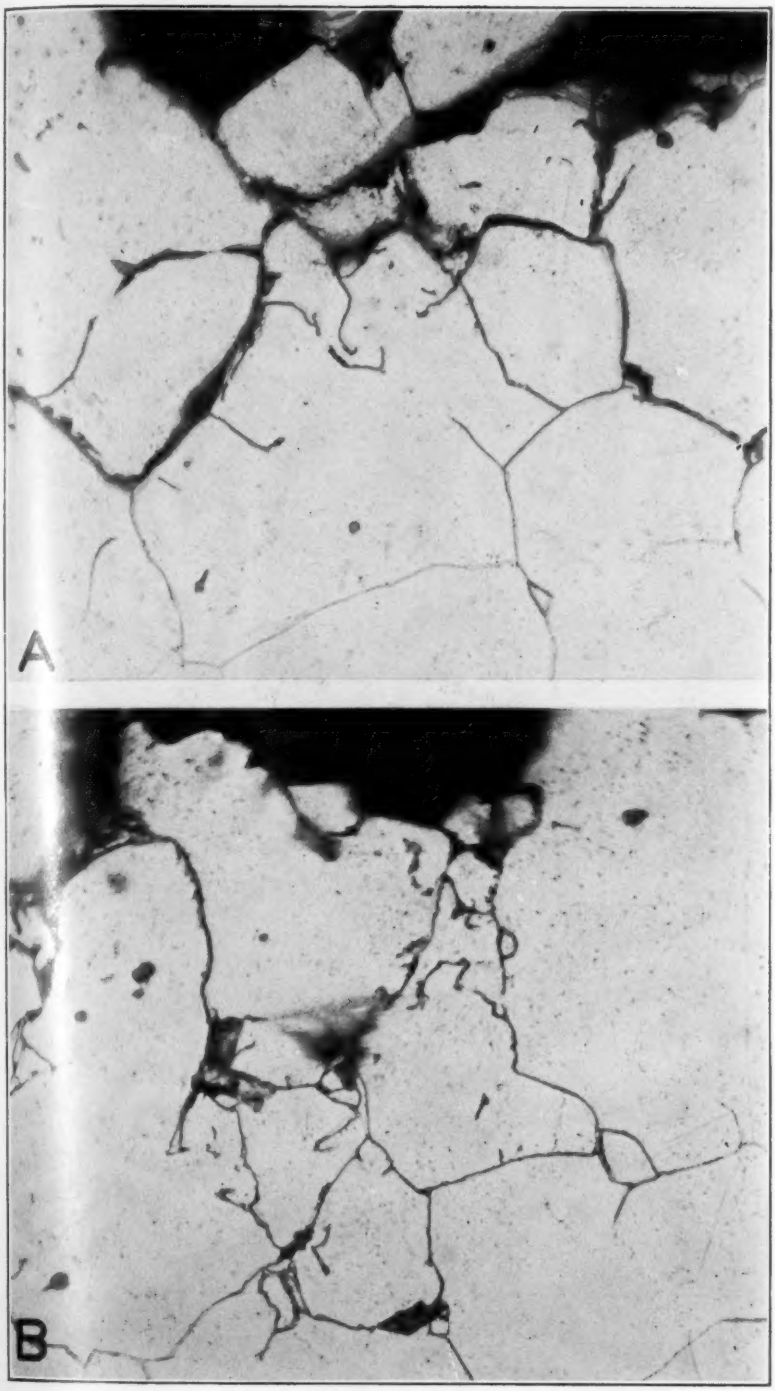

FIGURE 12.—*Edges of a specimen of plate metal, heat treated at 650° C and corroded in boiling nitric acid.*

Specimen subsequently etched electrolytically in 10-percent oxalic acid. Magnification, 500×.

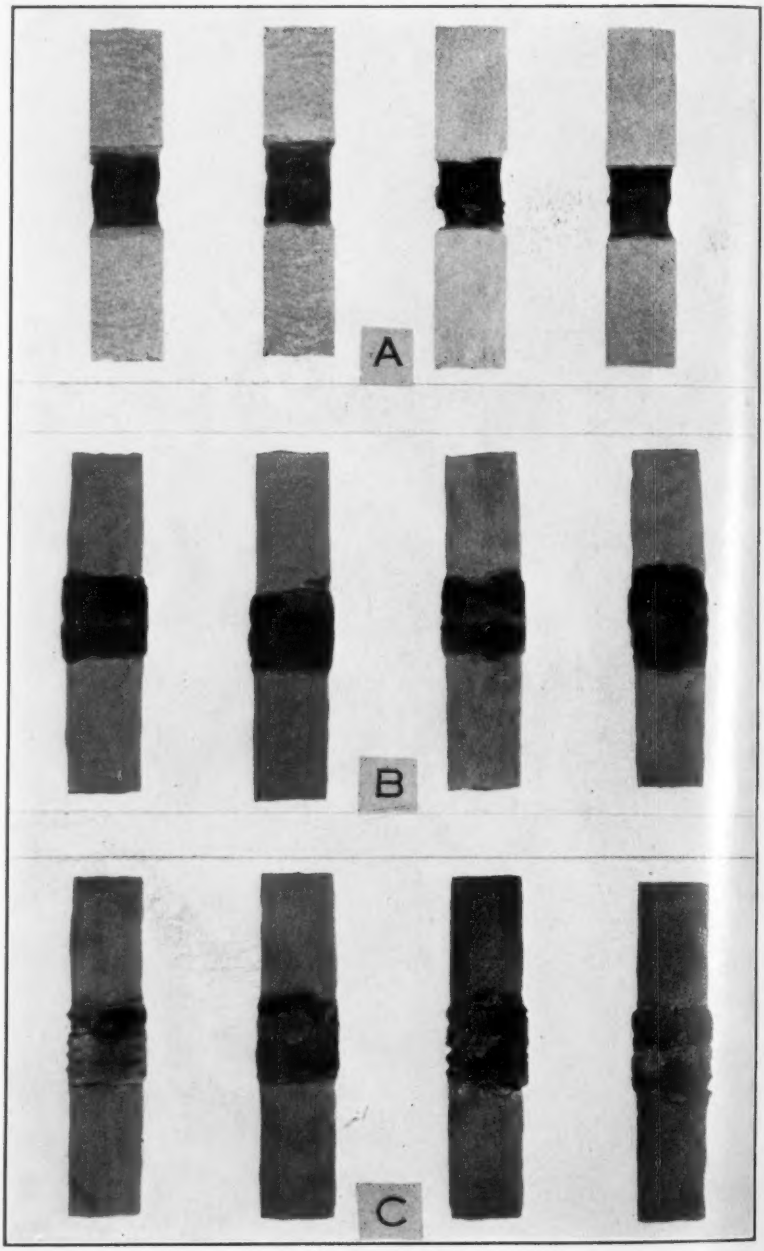

FIGURE 16.—*Specimens containing a single* V*-butt weld after corrosion in hydrochloric acid* ($\times 1$)

A. No heat treatment after weld was made.
B. Heat-treated at 650° C for 1 hour.
C. Heat-treated at 980° C for 1 hour.

These observations cannot be explained by the presence of carbide or its distribution, or by chromium depletion resulting from carbide formation. It is possible that these corrosion phenomena are connected with the presence of delta ferrite in the weld metal, but the connection is not obvious.

IV. SUMMARY

Concentrated nitric acid at its boiling point has previously been used to produce intergranular corrosion in stainless steel. Evidence was obtained that this type of corrosion is the result of the selective attack by the acid on carbides that exist as networks at the grain boundaries. The cohesion between the constituent grains is destroyed

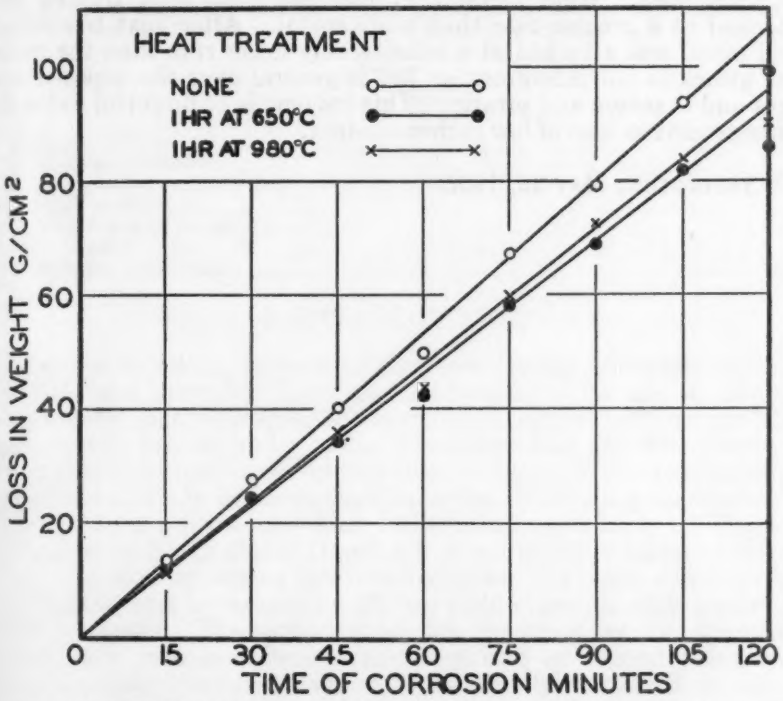

FIGURE 15.—*Corrosion of welded specimens in hydrochloric acid.*

and the material seriously weakened. Specimens of low-carbon stainless steel (0.06 percent of carbon) develop this type of intergranular corrosion only after the specimens have been heated so as to permit the formation of a carbide network at the grain boundaries. Without such heat treatment, the amount of the grain boundary carbides was not sufficient to render the steel subject to intergranular corrosion by boiling nitric acid.

A solution of copper sulphate in sulphuric acid has also been used to produce intergranular corrosion in stainless steels. It has been established by other investigators that the copper sulphate-sulphuric acid reagent does not destroy the carbides at the grain boundaries but, instead, attacks the adjacent metal that has been impoverished in

chromium through the formation of carbides. Low-carbon stainless steel (about 0.06 percent of carbon) is not subject to intergranular corrosion by this solution, presumably because the formation of carbides does not cause appreciable depletion of the chromium content of the metal adjacent to the boundaries.

Weld metal of approximately the same composition as the plate was not susceptible to intergranular corrosion in nitric acid or in a copper sulphate-sulphuric acid solution, regardless of heat treatment. Carbides were not found in the grain boundaries of specimens that had been heated to facilitate their formation, but were localized in delta ferrite pools scattered throughout the matrix.

Low-carbon stainless steel, exposed to the action of $6N$ hydrochloric acid, lost weight much more rapidly than in either of the other solutions used. Weld metal that had not been heat treated was attacked at a greater rate than plate metal. After heat treatment, weld metal was attacked at a considerably lower rate than the plate. The attack is not intergranular but is general over the exposed surfaces and is severe and erratic. This reagent is of doubtful value for testing stainless steel of low carbon content.

WASHINGTON, May 29, 1936.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP964

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

ANODIC COATING OF MAGNESIUM ALLOYS

By R. W. Buzzard and J. H. Wilson

ABSTRACT

Magnesium alloys may be anodized in a bath of sodium phosphate, ($NaH_2PO_4.H_2O$) and sodium dichromate, ($Na_2Cr_2O_7.2H_2O$). The film obtained combines both corrosion-resistance and paint-holding properties, without serious change of dimensions of the treated piece, even on machined surfaces.

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I. INTRODUCTION

Magnesium alloys, because of their low density and relatively high strength and ductility, have many advantages for use in aircraft. Noteworthy disadvantages, however, are their marked susceptibility to corrosive attack under saline conditions and the low degree of adherence of protective coatings to their surfaces. Numerous attempts have been made to improve their behavior by treating the surface so as to produce a protective film. A solution containing 1.5 lb/gal or 180 g/liter of $Na_2Cr_2O_7.2H_2O$ and 1.5 pt/gal or 190 ml/liter of HNO_3, sp gr 1.42, and known as the "chrome pickle" [1] [1] that was described by Winston and his associates [2] has yielded satisfactory results for many purposes. The surface condition produced by this treatment serves both as a retardant of corrosion and as a good paint base. However, this treatment cannot be satisfactorily applied to dimensioned machined surfaces, as it materially reduces the cross section. The alkaline chromate treatment [3] developed by Sutton and LeBrocq [4] can be used on machined surfaces but, according to tests by the present authors, it has not been found to give corrosion protection equivalent to that of the chrome-pickle treatment.

The remarkable success attained with the anodic oxidation or so-called "anodizing" of aluminum and its alloys prompted attempts to develop a similar treatment for magnesium, even though previous efforts to develop a satisfactory electrolytic treatment had not been very successful. A process has recently been perfected which combines in large measure the advantages of the chrome-pickle and the alkaline chromate treatments.

[1] Numbers in brackets refer to literature references at the end of the paper.

II. BATH COMPOSITION

Numerous experiments led to the selection of a bath containing about 10 percent of sodium dichromate, ($Na_2Cr_2O_7 \cdot 2H_2O$), and 2 to 5 percent of monosodium phosphate, ($NaH_2PO_4 \cdot H_2O$).

III. PROCEDURE

All parts must be carefully cleaned before being anodized. Electrolytic cleaning has been found very satisfactory. For example, the specimen is made the cathode for at least 3 minutes at 90° C (194° F) in a bath containing

Sodium carbonate (soda ash) (Na_2CO_3)____4 oz/gal (30 g/liter);
Trisodium phosphate ($Na_3PO_4 \cdot 12\ H_2O$____4 oz/gal (30 g/liter).

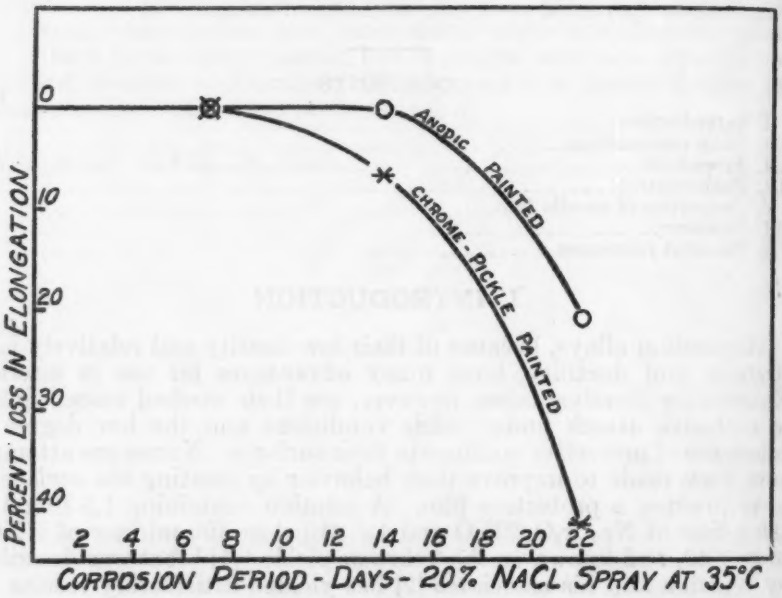

FIGURE 1.—*Relative value of anodic films as paint bases.*

A sufficient potential (usually 4 to 6 volts) is applied to produce a vigorous evolution of hydrogen around the specimen being cleaned. Steel plates are used as anodes.

The cleaned metal is then made the anode in the anodizing bath, in which the cathode is steel and a sufficient voltage is applied to produce a current density of 5 to 10 amperes per square foot of anode surface. The time necessary to produce a satisfactory coating is dependent on the composition of the alloy, the temperature of the bath, and the current density used; at 50° C it varies between 30 and 60 minutes.

Satisfactory results with most of the commercial alloys of magnesium have been obtained in this laboratory with a bath of the above composition, operated over a wide range of temperature and of current density. The permissible maximum current density is limited by the occurrence of pitting on the anode. As might be expected, as the

current density is increased, the time required to produce a good coating is lowered considerably. Satisfactory surface films have been obtained on an alloy of the magnesium-aluminum class (4.0% Al and 0.3% Mn) with current densities from 5 to 100 amperes per square foot and with temperatures from 30 to 80° C (86 to 176° F). The favorable conditions are more restricted for alloys of the magnesium-manganese type. A lower current density, preferably less than 10 amperes per square foot, was found necessary with an alloy having the nominal composition of 1.5% Mn and 98.5% Mg.

A satisfactory coating is smooth and adherent and does not flake on a sheet when bent at an angle of 90°. The color varies with the composition of the alloy treated, from a dirty green to a shiny black. The higher the aluminum content of the alloy, the darker is the film.

IV. BATH CONTROL

Satisfactory operation of this bath depends on the maintenance of proper hydrogen-ion concentration (pH). For the phosphate-dichromate bath described above, the pH should be maintained between 4.0 and 4.8. During operation of the bath, magnesium is dissolved and the pH rises. Phosphoric acid must then be added to restore the initial pH. A glass electrode has been found most satisfactory for measuring the pH.

Magnesium phosphate is only sparingly soluble in the phosphate-dichromate solution. As magnesium dissolves during the use of the bath, the saturation point of magnesium phosphate is reached, and a precipitate of this substance forms, which removes phosphate ion from the bath. The addition of the amount of phosphoric acid required to maintain the desired pH of the solution is not usually sufficient to maintain the necessary concentration of the phosphate ion. Additional sodium phosphate, in amounts determined by analysis of the bath, must therefore be added. The dichromate concentration changes very slowly with use, and an occasional analysis will indicate when more dichromate is necessary.

V. PROPERTIES OF ANODIC FILM

Corrosion tests by the salt-spray method have shown the anodic films to be equal in corrosion resistance to the surface coatings produced by chemical treatment. The method used was to determine the change in tensile properties, especially elongation, of strips of sheet material that were machined to tensile-bar dimensions after exposure to the salt-spray test. Salt-spray tests were made with a 20-percent solution of NaCl at 35° C, on a magnesium alloy (4.0 Al, 0.3 Mn), in sheet form 0.060 inch thick and having an average initial elongation of 12.4 percent. Exposure to salt spray for 5 days caused a loss of 63 percent in elongation on specimens that had been given the chrome-pickle treatment, and of 44 percent on anodized specimens. The chrome-pickle treatment was carried out in a fresh solution to assure the production of a film of the best quality.

TABLE 1.—*Loss in elongation of cast tensile bars of magnesium-aluminum alloys (percentage of initial elongation) (6.0 Al, 0.2 Mn, 3.0 Zn) after 10 days in 20-percent NaCl spray at 35° C*

[Initial elongation 7.8 percent]

Bar	Surface preparation	Loss of elongation
		Percent
1	Bare	32.0
2	Chrome-pickle—without previous cleaning	22.0
3	Anodized—without previous cleaning	10.0
4	Alkaline chromate—caustic cleaning	20.0
5	Chrome-pickle—caustic cleaning	4.0
6	Alkaline chromate—electrolytic cleaning	10.0
7	Chrome-pickle—electrolytic cleaning	23.0
8	Anodic—electrolytic cleaning	0

Cast tensile bars of magnesium alloy (6.0 Al, 0.2 Mn, 3.0 Zn) with an average initial elongation of 7.8 percent, were tested in the same manner for 10 days. In table 1 are shown the percentage losses in elongation for bars treated under different conditions. The anodic coating on bar 8 showed no corrosion on visual examination and no loss of elongation in the tensile test.

Salt-spray tests have shown that the anodic film is equal to chrome-pickled surfaces as a paint base. Specimens of magnesium-aluminum alloy (4 percent of Al, 0.3 percent of Mn) with two coats of aluminum-pigmented spar varnish applied to the bare surface, and also those painted after various surface treatments such as the fluoride [5] Parko (a phosphate dip), selenious acid (6) and chrome-pickle, showed failure on visual examination. Anodized specimens showed no failure in a similar test for the same periods.

For a comparison of chrome-pickled surfaces with anodic surfaces as paint bases, two sets of specimens were prepared, one of which was anodized and the other was chrome-pickled.[2] Both were then coated as follows:

One coat of zinc chromate primer was applied and baked for 1 hour at 225° F; one coat of surfacer was applied and baked for 1 hour at 225° F, and two successive coats of black baking enamel were applied and baked for 1 hour at 200° F.

After 3 weeks of exposure to salt spray the specimens were tested in tension. The chrome-pickled specimens suffered an average loss of 41 percent of the initial elongation, while the anodized bars showed a loss of only 21 percent.

Magnesium-aluminum alloy sheet that was weighed before and after the anodic treatment showed a loss in weight of the order of $0.1 g/dm^2$, which is about 1 percent of the weight. The measured loss in thickness did not, however, exceed 0.0001 inch, which is much less than that observed on chrome-pickled specimens.

VI. SUMMARY

Magnesium alloys can be coated by an anodic process. The films obtained combine corrosion-resistance and paint-holding properties, and the process causes no appreciable change of dimensions of the treated piece, even on machined surfaces.

[2] Chrome-pickled and painted by courtesy of the Dow Chemical Co., Midland, Mich.

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[3] Chemical treatment no. 3—Magnesium Base Alloys. Bureau of Aeronautics, Navy Department Spec. M–303, Pt. 2 (June 1, 1936).
[4] *The protection of magnesium alloys against corrosion.* H. Sutton and L. F. LeBrocq. J. Inst. Metals **57,** 199 (1935).
[5] P. Prier. U. S. Patent 1957354. (May 1, 1934.)
[6] G. D. Bengough and L. Whitby. British Patent 378916 (May 1, 1934.)
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[9] Dowmetal. The Dow Chemical Co., Midland, Mich. (1935).
[10] *Light alloy for aeronautical purposes with special reference to magnesium alloys.* L. Aitchison. J. Royal Aero. Soc. no. 281, **38,** 382 (May 1934).
[11] *Magnesium alloy protection by selenium and other coating processes.* G. D. Bengough and L. Whitby, J. Inst. Metals **48,** no. 1, 147 (1932); J. Soc. Chem. Ind. **50,** 835 (1931).

WASHINGTON, October 19, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP965

Part of Journal of Research of the National Bureau of Standards, Volume 18, January 1937

PRESSURE LOSSES FOR FLUID FLOW IN CURVED PIPES

By Garbis H. Keulegan and K. Hilding Beij

ABSTRACT

This paper presents the results of a study of the flow of water in smooth-walled, large-radius curved pipes for the viscous and turbulent regimes over a range of Reynolds numbers from 500 to 60,000. The discussion is based on data obtained with ¾-inch brass tubing. Two series of tests were made. In the first series pressure losses were measured on ten bends, and simultaneous measurements were made on the downstream tangents. In the second series pressure losses were measured on four equal segments on each of four bends.

The greater part of the paper is devoted to a consideration of the results in the viscous flow regime. In this part of the investigation care was taken to assure parabolic velocity distribution, or nearly so, at the entrance of the bends. Empirical formulas are given for the effective resistance coefficient of an entire bend and for the downstream tangent. A method of computing to a first approximation the length of curve required for the establishment of the velocity distribution characteristic of a curved pipe is presented.

Critical numbers for bends of different curvature ratios when the entering flow is laminar are briefly discussed. Average values for the relative increase in resistance in a bend as compared with straight pipe in the regime of turbulent flow are given for the range of Reynolds numbers from 40,000 to 60,000.

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I. INTRODUCTION

A *curved pipe* or *pipe bend*, in the restricted sense used in this paper, is a pipe of circular cross section bent to the form of a circular arc. The straight pipes that connect to the two ends of the bend always lie in the plane of the bend, as is implied by the terms, *upstream tangent* and *downstream tangent*, used in this paper.

When a fluid flows under pressure through a straight horizontal pipe, the pressure decreases in the direction of flow as a consequence of the energy loss resulting from fluid friction. A thin layer of the fluid adheres to the wall of the pipe and remains at rest with respect to it. Thus the velocity of the fluid at any cross section increases from zero at the wall to a maximum at the axis of the straight pipe. If fully

developed laminar [1] flow exists, the curve obtained by plotting velocity against distance from the pipe axis (called the *velocity distribution curve* or the *velocity profile*) is a parabola, and the loss of energy is brought about by the viscous resistance to sliding of concentric layers of the fluid over each other. If the flow is turbulent, the loss of energy is greater and is due mainly to turbulent mixing of the fluid. In this case the velocity profile is flatter near the axis of the pipe and steeper near the wall than it is for laminar flow.

Now if the pipe is curved instead of straight, the velocity profile will no longer be symmetrical about the axis of the pipe. Centrifugal force due to the change in direction of the flow sets up secondary currents in the plane of the cross section, with the result that the maximum velocity is no longer at the center of the section but at some point intermediate between the center and the wall. It is found, as might be expected, that this distortion of the velocity profile is accompanied by larger pressure losses along the pipe than occur for the same flow with the symmetrical profile that is characteristic of a straight pipe. Hence a curved pipe always offers more resistance to the flow of a fluid than would the same pipe if straight. At very small Reynolds numbers, however, the difference is so slight, that it cannot be measured by the methods ordinarily employed.

In the present experiments, the water was brought into the upstream tangent through a bell-shaped entrance. As is well known, such an entrance tends to produce uniform velocity distribution over the cross section at its exit. However, as the water flows along the straight pipe comprising the upstream tangent, this flat velocity profile changes, gradually assuming the form that is characteristic of the straight pipe, until a point is reached, if the pipe is long enough, beyond which this characteristic profile persists unchanged throughout the remainder of the length of the straight pipe. The portion of the pipe in which the velocity profile changes from one definite form to another form, characteristic of the pipe in question, is called the *transition segment*, and the length of this segment is called the *transition length*.

Since the velocity profile that exists at the entrance to the bend is not the characteristic form for the curved pipe, however, another readjustment takes place in the bend, and if the latter is long enough, a new velocity profile that is characteristic of the curved pipe and the existing flow conditions will become established some distance downstream from the entrance to the bend, and will persist unchanged to the downstream end of the bend. The terms *transition segment* and *transition length* are applicable to the bend as well as to the straight pipe. It was also found convenient to distinguish between *long* bends—those which are longer than the transition length, and *short* bends—those which are shorter than the transition length.

Another readjustment of the velocity profile takes place in the downstream tangent just below the bend, since the profile characteristic of the bend must now change back to that characteristic of the straight pipe.

It is evident, therefore, that we cannot confine our attention to the bend alone in considering the total loss of pressure caused by a bend, for the pressure loss in the transition segment of the bend depends on the particular velocity profile at the bend entrance, and this is deter-

[1] Throughout this paper the term *viscous flow* will be used to designate flow at Reynolds numbers below the critical. While viscous flow is *laminar* in straight pipes, it is not so in curved pipes, because of the secondary currents which result from the curvature.

mined by the conditions in the upstream tangent. Also the pressure loss in the transition section of the downstream tangent will be greater than that in an equal length of straight pipe in which fully developed laminar velocity distribution prevails. This excess pressure loss that occurs in the transition segment of the downstream tangent is due to the readjustment of the velocity distribution that takes place here.

The loss of pressure in any pipe, straight or curved, is given by the relation

$$\frac{1}{\gamma}\frac{\Delta p}{\Delta x}=\lambda\cdot\frac{l}{d}\cdot\frac{U^2}{2g} \tag{1}$$

where

γ=the specific weight of the fluid,
Δp=the pressure drop at the axis of the pipe over an axial length Δx,
λ=the coefficient of resistance,
d=the pipe diameter,
U=the mean of the velocity components parallel to the axis in a cross section, and
g=the acceleration of gravity.

When the velocity distribution is the same for all cross sections, as in straight pipes or bends downstream from the adjustment length, the pressure drop, Δp, is the same for all elementary lengths, Δx, and the coefficient of resistance is constant along the pipe for any given flow. Under these conditions, for a smooth straight pipe, the resistance coefficient is a function of the Reynolds number only, the Reynolds number being defined by

$$R_e\equiv\frac{dU}{\nu},$$

where ν is the kinematic viscosity of the fluid. For laminar flow we have

$$\lambda=64/R_e, \tag{2}$$

and for turbulent flow, below a Reynolds number of about 130,000, the empirical relation

$$\lambda=CR_e^{-1/4}, \tag{3}$$

where C, as experimentally determined, has a value in the neighborhood of 0.31.

When the velocity distribution varies from section to section, as in any transition segment, the pressure drop also varies, and hence the coefficient of resistance at any given flow is different for all elementary lengths, Δx.

As the coefficient of resistance is determined experimentally by the application of equation 1, it is necessary to measure the pressure in the axis of the pipe at any two given cross sections in order to determine the pressure drop Δp. If the directions of the absolute velocities at all points in a cross section are parallel to the pipe axis, then the pressure is constant over the entire cross section. It may, therefore, be measured at any point in the section and, in particular, at the wall of the pipe.

In a curved pipe, because of the curvilinear paths of the moving fluid particles, the pressures, p_i and p_o, at the inner and outer ends, respectively, of a diameter in the plane of the curve are not equal. At the ends of a diameter normal to the plane of the bend of the pres-

sures, p_n, are equal on account of symmetry. However, if the radius of curvature of the bend is large compared with the pipe diameter, then

$$p_i+p_o=2p_n, \tag{4}$$

a fact which was verified by Richter[2] for turbulent flow. Undoubtedly it applies to viscous flow also. It is generally assumed by experimenters that when equation 4 holds, the mean pressure in a cross section is given by $(p_i+p_o)/2$, or by p_n, and this mean pressure may be taken as the axial pressure, with negligible error. Accordingly, in this investigation pressures were measured either by averaging the pressures at the two ends of the diameter normal to the plane of the bend, or by averaging these two and also those at the ends of the diameter in the plane of the bend.

1. PREVIOUS WORK

There are very few reported investigations, either theoretical or experimental, on flow in long pipe bends. The theoretical treatment for viscous flow is complicated so greatly by the existence of secondary currents arising from the centrifugal action of the curvilinear flow that no general rigorous solution has been obtained. The first attempt at a theory was made by Dean.[3] Although he made but little progress toward the derivation of a theoretical expression for flow in bends, his analysis proved to be very valuable in subsequent work for two reasons. A first result of his analysis related to the law of similarity for mean velocities in curved pipes. His original mathematical statement of the law can be simplified if we introduce the shear velocity in place of the pressure gradient. The law can then be stated as follows: for a given shear the ratio of the mean velocities in two pipes of the same dimensions, one straight and the other curved, depends on a parameter given by the product

$$\left(\frac{U_* d}{\nu}\right)^2\left(\frac{d}{D}\right)^{1/2},$$

where

$U_*=(\tau/\rho)^{1/2}$ is the shear velocity,
τ=the mean shear at the wall,
ρ=the density of the fluid,
d=the diameter of the pipe,
D=twice the radius of the bend, and
ν=the kinematic viscosity of the fluid.

(It is convenient to call the ratio d/D the *curvature ratio* of the bend.) However, White[4] found it more convenient to apply the converse of the above law. The converse law can be stated: for a given mean velocity in two pipes of the same dimensions, one straight and the other curved, the ratio of the resistances depends on a parameter given by the product of the Reynolds number and the square root of the curvature ratio; that is, $R_e.(d/D)^{1/2}$. With this as a starting point White was able to correlate the results of his experiments. The relative increase of resistance due to curvature was found to be a

[2] H. Richter, *Der Druckabfall in glatten gekrümmten Rohrleitungen.* Ver. deut. Ing. Forsch. Heft 338 (1930).
[3] W. R. Dean, *The streamline motion of fluid in a curved pipe.* Phil. Mag. [7] **4**, 208 (1927); **5**, 673 (1928).
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function of $R_e.(d/D)^{1/2}$ provided the flow in the bends did not become turbulent.

The second result of Dean's analysis was an explanation of the manner in which two symmetrical circulations or secondary currents are set up in a bend. Taylor's[5] study of the onset of turbulence in curved pipes was based on the existence of these secondary currents. The introduction of dyes through perforations at the ends of a horizontal diameter of a bend made the secondary currents visible, and the disturbance of these currents formed a satisfactory criterion for the onset of turbulence. Eustice's[6] method of introducing dyes at the entrance of the bend had previously proved unsuccessful.

Considerable information is given by Adler[7] on the distribution of axial velocities both for viscous and for turbulent flows. After obtaining experimental data on the nature of the flow in the central core, he gives an interesting derivation of an expression for the resistance coefficient for viscous flow at large values of $R_e.(d/D)^{1/2}$ by making use of the Prandtl boundary layer theory.

2. SCOPE OF PRESENT INVESTIGATION

The results of the above-mentioned investigations on resistance coefficients for viscous flow in long bends apply only to segments of bends downstream from the transition segment. The chief purpose of the investigation which forms the subject of this paper was to furnish the data required for calculating the total resistance due to a long bend. It was necessary, therefore, to determine the effective resistance coefficient for the complete bend including the transition segment, and also the effect of the bend on the resistance coefficient of the downstream tangent.

The critical number (the Reynolds number at which viscous flow becomes unstable and changes to turbulent flow) was determined for each bend. Data were obtained for turbulent flow up to the maximum flow possible with the apparatus, which corresponded to a Reynolds number of about 60,000.

II. APPARATUS

The water supply system is shown in figure 1. For low flows (below the critical), the constant level tank was used to supply water under a constant head. For the higher flows, water was drawn directly from the city mains at a pressure of about 30 lb /in^2. By the use of the surge tank, the effects of sudden and severe pressure changes in the supply from the city mains were reduced considerably, but they could not be altogether eliminated. To insure minimum disturbance of the flow at the entrance to the experimental pipe, the supply line was increased from a 3-inch diameter in the vertical portion by means of an expander and an expanding elbow to a diameter of 8 inches in the pipe forming the supply chamber. The entrance cone of the experimental pipe was mounted at the center of a flange on the end of the 8-inch pipe. A valve at the end of the exit pipe was used to control the flow. Below the valve was a pocket for the thermometer and a swinging gooseneck for diverting the flow from the waste line to the measuring tank. The thermometer was gradu-

[5] G. I. Taylor, *The criterion for turbulence in curved passages.* Proc. Roy. Soc. (London) **124,** [A] 243 (1929).
[6] J. Eustice, *Flow of fluids in curved passages.* Engineering **120,** 604 (1925).
[7] M. Adler, *Strömung in gekrümmten Rohren.* Z. ang. Math. u. Mech. **14,** 257 (1934).

ated in 0.2° C, and was read to the nearest 0.1° C. A volumetric tank, calibrated by weighing, with a float gage connected to a pointer indicating on a dial face, was used for measurement of flow. Times were measured with a stop watch.

Measurements of head were made by means of water manometers for the lower flows and mercury manometers for the higher flows. Capillary tubes were used to damp out the manometer oscillations to the point where they were barely noticeable. Another purpose of the capillary tubes was to preserve the stability of viscous flow in the test line. At Reynolds numbers above 3,000, slight pressure oscillations caused flow into and out of the piezometer openings when capillaries were not used, and the resulting disturbance often was sufficient to bring on turbulence in the test pipes. All manometer readings were made to the nearest 0.1 mm by means of a cathetometer.

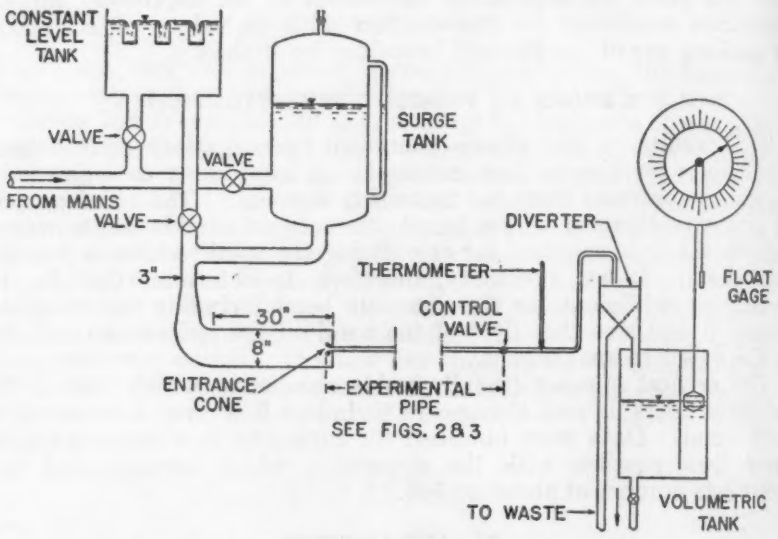


FIGURE 1.—*Arrangement of experimental apparatus.*

III. EXPERIMENTAL PIPES

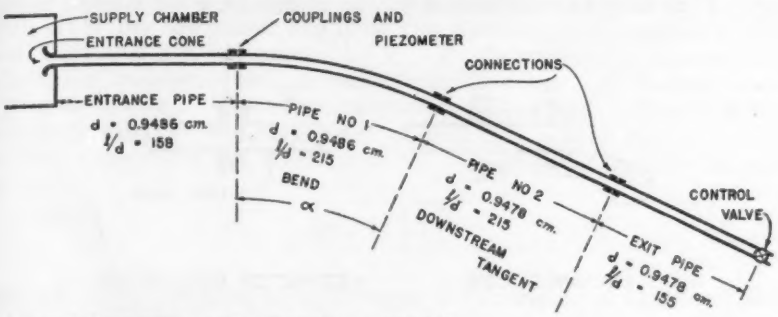
All the experimental pipes were of smooth, drawn-brass tubing, of nominal ⅜-inch internal diameter, specially selected for straightness and uniformity of bore. The lengths, measured internal diameters, and arrangement of the pipes are shown in figure 2.

Effective pipe diameters were determined by weighing the amount of water necessary to fill the pipe completely. Uniformity of cross section was determined by measuring outside diameters by micrometer gages, assuming a uniform wall thickness.

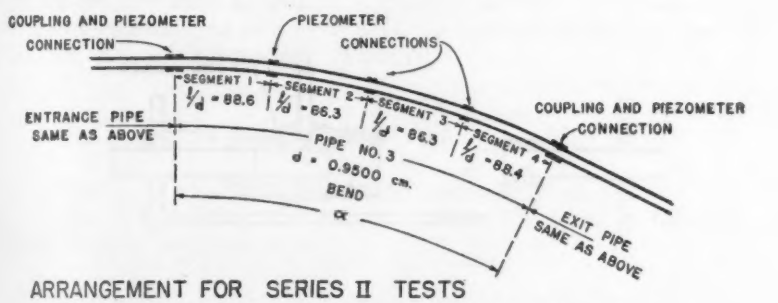
The critical number for a bend increases with increasing curvature ratio, so that above a certain Reynolds number it is possible for turbulent flow to exist in the entrance pipe and the upstream end of the bend, with viscous flow existing in the downstream end of the bend. (See section V.) As it was desired to exclude this condition from the scope of the investigation, special precautions were necessary in the design of the entrance pipe. Now, the critical number for a bend of

the largest curvature ratio to be tested was known from the work of other experimenters to be in the neighborhood of 5,000 (see fig. 12), so that an entrance pipe was required having a critical number of at least 6,000. This condition was realized by using the bell-shaped entrance cone shown in figure 3, connected to a long entrance segment of straight pipe, shown in figure 2.

Two series of tests were made. In the first series, resistance coefficients for two pipes, no. 1 and 2 in figure 2, were measured. All the bends were formed from pipe no. 1, which, for each test, was bent elastically into a circular arc of the curvature ratio desired. Pipe no.



ARRANGEMENT FOR SERIES I TESTS



ARRANGEMENT FOR SERIES II TESTS

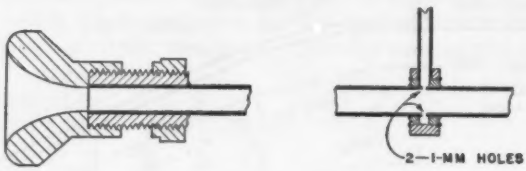
FIGURE 2.—*Experimental pipes with pipe dimensions.*

2 was always kept straight and connected to the downstream end of the bend. In the second series, resistance coefficients were determined for four approximately equal segments of pipe no. 3 (fig. 2) which was bent elastically to form the bends.

In order to determine the deformations of the pipes caused by bending, the following procedure was used. A pipe of the same material and dimensions as those used in the tests was closed at one end and this end clamped to a table. At the fixed end was attached a vertical glass tube of 0.5-mm bore. The pipe was then completely filled with water and the free end closed. Next the pipe was bent into horizontal arcs of various curvatures and the corresponding rise of water in the glass capillary was determined. The relative decrease of internal volume ($\Delta V/V$) due to bending appeared to vary as the square of the curvature: for $d/D=69.7\times10^{-4}$, $\Delta V/V=7.8\times10^{-4}$. The external diameters at the midpoint of the pipe were also meas-

ured for this curvature. The vertical diameter increased by 0.004 d; while the horizontal diameter (in the plane of the arc) decreased by 0.006 d. These measurements indicate a decrease in effective diameter of about 1 part in 1,000. It was assumed that these changes of form were sufficiently small so that no correction was required for deformation of the pipes.

The experimental pipes were connected by special couplings, the details of which are shown in figure 3. With this arrangement, every joint could be inspected easily. In each coupling were four piezometer openings 1 mm in diameter, connecting to a piezometer ring. This ring was connected to the manometer by copper tubing.



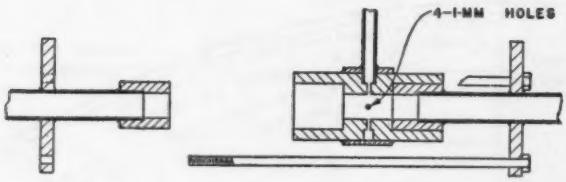


FIGURE 3.—*Fittings for experimental pipes.*

In addition to the couplings at the ends, pipe no. 3 was provided with three sets of piezometer openings as shown in figure 2. Each set consisted of two 1-mm holes on the vertical diameter connected to a piezometer ring.

IV. EXPERIMENTAL RESULTS FOR VISCOUS FLOW

The results of the series *I* tests on the bends formed from pipe no. 1 are given in figures 5, 6, 13, 14, and 15, and on the downstream tangent, pipe no. 2, in figures 9, 10, 13, 14, and 15. The results of the series *II* tests on the bends formed from pipe no. 3 are given in figures 4 and 7. In each figure the data are presented in a manner conforming to the analysis of the results in the following discussions.

1. RESISTANCE IN BENDS, INCLUDING TRANSITION SEGMENT

The following discussion applies to viscous flow with parabolic or nearly parabolic velocity distribution at the entrance of the bend. The resistance coefficient at the entrance, therefore, is the same as that for a straight pipe. Denote this coefficient by λ_s.

At a certain axial distance x_1, measured from the entrance to the bend, the velocity distribution assumes a pattern which is characteristic of the bend, and which persists from this point to the end of the bend. The distance x_1 is thus the transition length, and the corresponding portion of the bend is the transition segment. Downstream from the transition segment the coefficient of resistance will be constant and will be denoted by λ_c. In the transition segment the coefficient of resistance will increase from its value λ_s at the entrance to its value λ_c at x_1. The effective coefficient λ_x of any segment of the bend (beginning at the entrance) of length x where $x_1<x<l$ will, therefore, vary with x. This effective coefficient is defined by the relation

$$\frac{1}{\gamma}\Delta p=\lambda_x\frac{x}{d}\frac{U^2}{2g}, \tag{5}$$

where Δp is the pressure loss between the entrance of the bend and the point at distance x downstream, d is the pipe diameter, U is the mean velocity, and g is the acceleration of gravity. In general, we should anticipate that λ_x will be a function of x/d, the relative length of the bend segment, as well as of d/D, the curvature ratio of the bend, and R_e, the Reynolds number. That is:

$$\lambda_x=\text{funct.}\left(\frac{x}{d}, \frac{d}{D}, R_e\right). \tag{6}$$

The problem is to evaluate this functional relationship.

Evidently, considering the resistance coefficient as a function of the bend length, we may write

$$\lambda_x.x=\int_0^{x_1}\lambda_a dx+\lambda_c(x-x_1), \tag{7}$$

where λ_a is the resistance coefficient for an infinitesimal length dx of the bend at any point $x=a$ in the transition segment, i. e., $0<a<x_1$. Hence λ_a is a local coefficient applying only to the point a, while λ_x, the effective resistance coefficient, is an average value for a length x of bend, where $x>x_1$, and λ_c is constant for the bend segment between the points x_1 and x. Since the terminal values of λ_a are λ_s at $x=0$, and λ_c at $x=x_1$, the integral in equation 7 may be replaced by

$$\int_0^{x_1}\lambda_a dx=k_x(\lambda_c-\lambda_s)x_1+\lambda_s x_1. \tag{8}$$

From equations 7 and 8,

$$\lambda_x.x=k_x(\lambda_c-\lambda_s)x_1+\lambda_s x_1+\lambda_c(x-x_1),$$

which on rearrangement and division by d becomes

$$\frac{\lambda_c-\lambda_x}{\lambda_c-\lambda_s}\cdot\frac{x}{d}=(1-k_x)\frac{x_1}{d}. \tag{9}$$

Writing for convenience,

$$(1-k_x)\frac{x_1}{d}\equiv\beta, \tag{10}$$

and dividing the numerator and denominator of the left-hand member of equation 9 by λ_s, we have

$$\frac{\frac{\lambda_c}{\lambda_s}-\frac{\lambda_x}{\lambda_s}}{\frac{\lambda_c}{\lambda_s}-1}\cdot\frac{x}{d}=\beta. \tag{11}$$

The two unknown quantities, k_x and x_1, are thus combined in the single unknown quantity β. In order to determine from equation 11 the dimensionless quantity β as a function of the Reynolds number R_e and the curvature ratio d/D it is necessary to find the values of the three resistance coefficients:

$$\lambda_s, \lambda_c, \text{ and } \lambda_x.$$

The value of λ_s, when the velocity distribution is parabolic, follows from Poiseulle's law and, as previously stated, is given by

$$\lambda_s=64/R_e. \tag{2}$$

The results of the initial experiment of the series *I* tests, for which pipe no. 1 was kept straight, agreed within small experimental errors with the relation (equation 2) up to a Reynolds number of about 4,500. At higher Reynolds numbers the experimentally determined values of λ_s became progressively greater than those given by equation 2, as shown in the upper left-hand graph in figure 13. Taking a Reynolds number of 7,000 for the purpose of comparison, we find that λ_s by equation 2 is equal to 0.00914, while the observed value for pipe no. 1 is 0.0102.

According to Schiller's method of computation [8] for the transition segment of a straight pipe, the effective coefficient for pipe no. 1 at a Reynolds number of 7,000 should be 0.00924. The difference between this result and the experimental value is far too large to be accounted for by experimental errors, so that only a small part of the discrepancy can be attributed to the fact that the entrance pipe was too short at the higher Reynolds numbers.

In his original paper Schiller [9] states that a very slight deviation from absolute straightness of his experimental pipe produced considerable changes in resistance. This clue affords a possible explanation of the high values of λ experimentally determined.

[8] See p. 25, et seq., in Prandtl-Tietjens, Applied Hydro- and Aero-Mechanics, (McGraw-Hill Book Co., New York, N. Y., 1934).

[9] L. Schiller, *Untersuchungen über laminare und turbulente Strömung*, Ver. deut. Ing. Forsch. Heft 248 (19.2).

From the graph in figure 4 we can compute approximately the curvature of pipe no. 1 necessary to give a value of $\lambda=0.0102$ at a Reynolds number of 7,000. We have

$$\frac{\lambda}{\lambda_s}=\frac{0.0102}{0.00914}=1.12,$$

and hence, by figure 4,

$$R_e\left(\frac{d}{D}\right)^{1/2}=30, \text{ approximately.}$$

As $R_e=7{,}000$, and $d=0.95$, we find

$$D=55{,}000 \text{ cm.}$$

If pipe no. 1 were bent to an arc of this diameter, the distance between the arc and the chord at the center-point of the arc would be about 2 mm. There was no sag in the pipe, since it was continuously supported, and in the horizontal plane there certainly was no deviation of more than 0.5 mm from a straight line. But if the pipe were sinuous, say forming two arcs of 55,000 cm diameter, then the maximum deviation from a straight line would be only about 0.5 mm. It is quite possible, therefore, that an apparently insignificant residual curvature in the pipe was sufficient to account for the high resistance coefficients observed.

As any such residual curvature would be inappreciable in comparison with the relatively large curvature imposed on pipe no. 1 when the bends were formed, the value of λ_s from equation 2, that is, for a truly straight pipe, is the proper one to use in equation 11.

White and Adler (see footnotes 4 and 7) have determined λ_c as a function of Dean's parameter, $R_e(d/D)^{1/2}$. However, it was decided to make a new determination of λ_c (see fig. 4), in order that all data of this investigation might be derived from the same source and might, therefore, be on a strictly comparable basis. The series *II* tests were made for this purpose, the experimental layout being that shown in figure 2.

An examination of the data showed that the resistance coefficients of the two segments furthest downstream (segments 3 and 4) were the same for all of the tests and larger than the corresponding coefficients for segment 1. The coefficients for the segment 2 were slightly smaller than those for the two downstream segments in some of the tests. It was judged that the two downstream segments were not appreciably affected by entrance effects. Accordingly, the resistance coefficient for the downstream half of the bend (segments 3 and 4) was taken as the value of λ_c and was computed from an equation similar to equation 1. The results are given in figure 4, where the ratio λ_c/λ_s is plotted as a function of $R_e.(d/D)^{1/2}$. These values are from 1 to 2 percent lower than those of White (see footnote 4).

From the same series of tests, values of λ_x were determined for two segment lengths, segment 1 alone and segments 1 and 2 combined, that is for values of x/d equal to 88.6 and 174.9, respectively. From the first series of tests values of λ_x were determined for 10 different curvatures, all of the same segment length, $x/d=215$. The results of

these two series of tests are given in figures 5, 6, and 7, in which the ratios λ_x/λ_s are plotted as a function of the Reynolds number.

The data in figures 4 to 7 may now be used to compute β by means of equation 11. If β is independent of the Reynolds number, then it should be possible to fit a curve corresponding to a constant value of β to each of the sets of points in figures 5, 6, and 7. Accordingly, a tentative curve was drawn through each set of test points, and values of λ_x/λ_s were read from each curve for about a dozen Reynolds numbers. The corresponding values of λ_c/λ_s were obtained from the curve in figure 4. Then values of β were computed, using equation 11. A second approximation (in some few cases a third) by shifting slightly

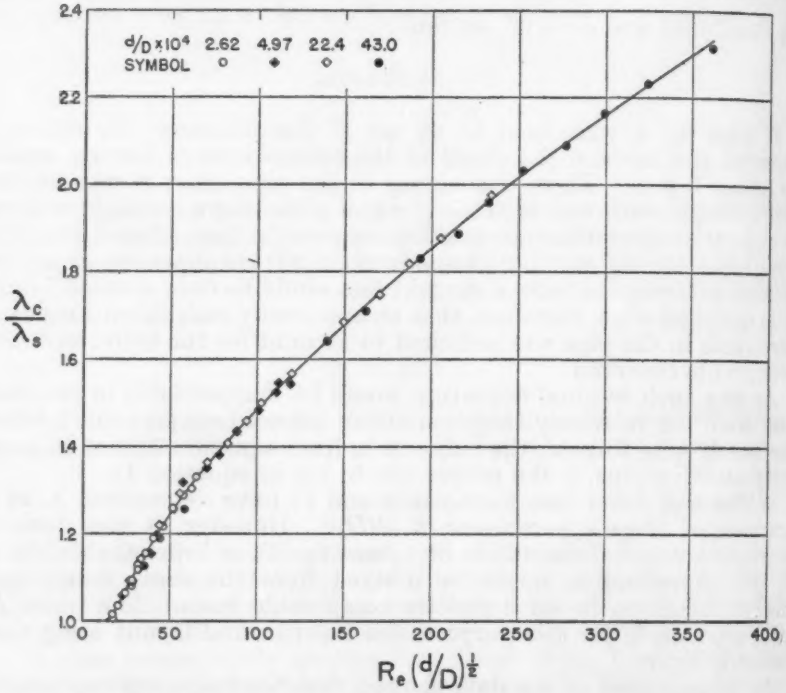


FIGURE 4.—*Ratio of the bend coefficient, λ_c, to the straight pipe coefficient, λ_s, as a function of $R_e(d/D)^{\frac{1}{2}}$.*

the tentative curves, sufficed to give practically constant values of β for each set of test points, i. e., for each bend. The final values adopted for β are given in table 1, and the corresponding curves are drawn in figures 5, 6, and 7. These curves appear to fit the data better than did the original tentative curves. The satisfactory agreement of the curves with the experimental points shows that β may be regarded as independent of the Reynolds number, within the limits of experimental error.

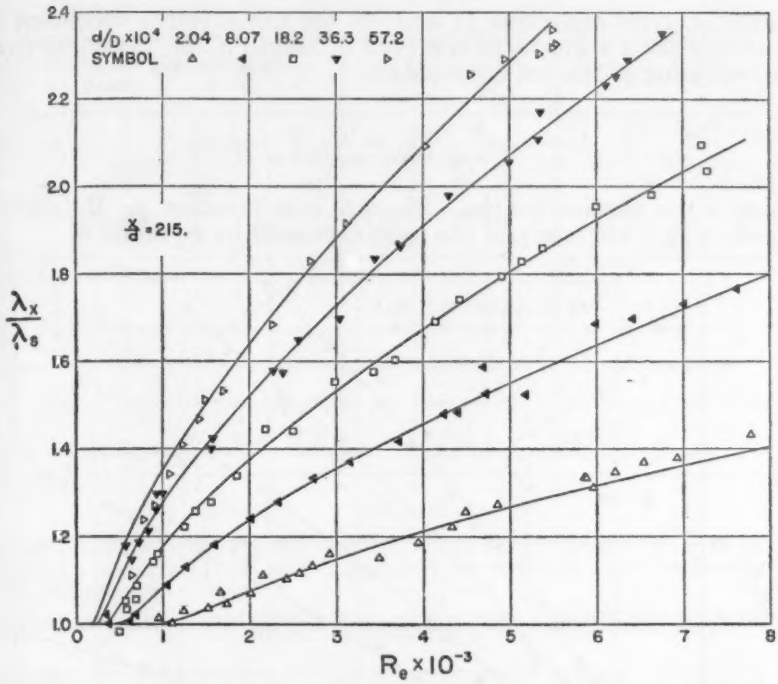


FIGURE 5.—*Ratio of the effective bend coefficient, λ_x, for bends of relative length $x/d=215$, to the straight pipe coefficient, λ_s, as a function of Reynolds number.*
The points represent experimental values and each curve represents a constant value of β as given in table 1. See also figures 6 and 7.

TABLE 1.—*Relation between β and the curvature ratio d/D*

d	x/d	$d/D\times10^4$	$(d/D)^{1/2}\times10^3$	β	$1/\beta$
cm		2.04	1.43	54.9	0.0182
		4.45	2.12	42.7	.0234
		8.07	2.84	33.3	.0300
		12.8	3.58	26.0	.0384
0.949	215.0	18.2	4.27	23.3	.0429
		24.2	4.92	21.5	.0465
		36.3	6.03	17.5	.0570
		45.3	6.73	16.2	.0618
		57.2	7.56	14.2	.0702
		69.7	8.35	13.0	.0768
		2.62	1.62	50.0	.0200
.950	88.6	4.97	2.23	41.3	.0242
		22.4	4.73	22.2	.0450
		43.0	6.56	16.2	.0617
		2.62	1.62	54.3	.0184
.950	174.9	4.97	2.23	40.5	.0247
		22.4	4.73	21.6	.0462
		43.0	6.56	16.8	.0596

From the results given in table 1, a simple empirical relationship between β and the curvature ratio d/D was found by plotting $1/\beta$ as a function of $(d/D)^{1/2}$, as shown in figure 8. The points in this figure are represented very satisfactorily by the straight line given by the equation

$$1/\beta=0.0059+0.844(d/D)^{1/2}. \tag{12}$$

Finally, from equations 11 and 12, for the effective coefficient of resistance for a segment of the bend of length $x > x_1$, measured from the beginning of the bend, we obtain

$$\lambda_x = \lambda_c - \frac{d}{x} \cdot \frac{(\lambda_c - \lambda_s)}{(0.0059 + 0.844(d/D)^{1/2})}, \tag{13}$$

which is the relation sought. Since λ_c is a function of $R_c.(d/D)^{1/2}$, equation 13 is obviously of the form expressed by equation 6.

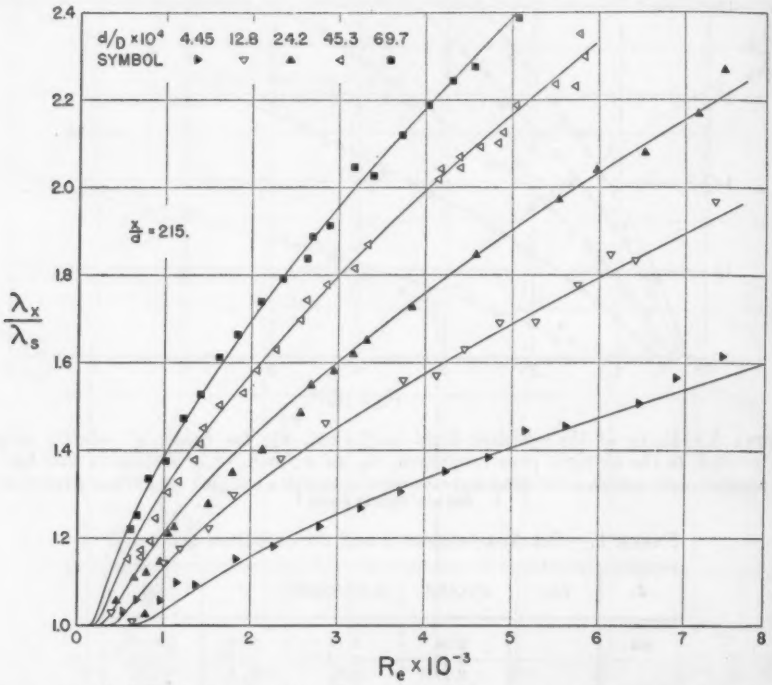


FIGURE 6.—*Ratio of the effective bend coefficient, λ_x, for bends of relative length $x/d = 215$, to the straight pipe coefficient, λ_s, as a function of Reynolds number.*

The points represent experimental values, and each curve represents a constant value of β as given in table 1. See also figures 5 and 7.

2. THE TRANSITION SEGMENT OF A BEND

The length x_1 of the transition segment of a bend cannot be derived from any experimental data known to the authors. All that is known from this investigation is that β, and hence $(1-k_x)x_1$, is independent of the Reynolds number and is a function of the curvature ratio d/D. If k_x should prove to be independent of the Reynolds number, then x_1 would be also. To settle this point effectively, experimental data must be obtained for a series of values of $x < x_1$. In order to obtain head losses large enough to be accurately measured, x_1 must be large. At the same time, d/D must include at least the range of values covered in the present experiments, and hence x_1/d must be approximately of the same magnitude as in the present experiments. Therefore, pipes of considerably larger diameter are required. As the

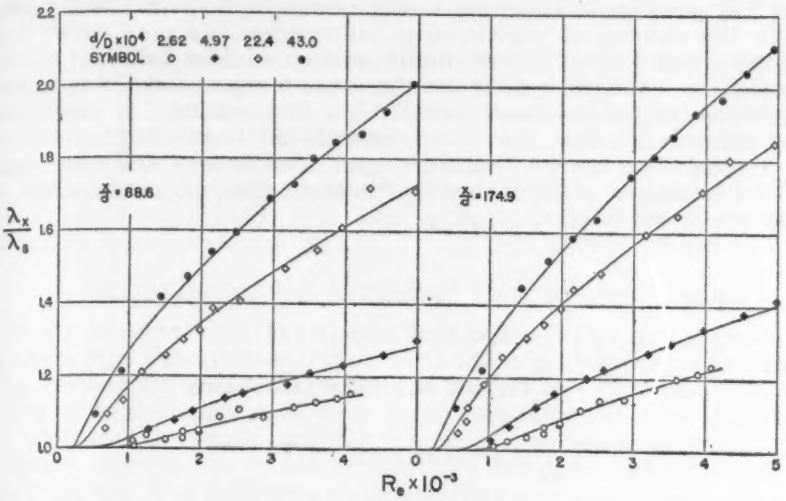


FIGURE 7.—*Ratio of the effective bend coefficient, λ_x, for bends of relative lengths $x/d=88.6$ and $x/d=174.9$, to the straight pipe coefficient, λ_s, as a function of Reynolds number.*

The points represent experimental values, and each curve represents a constant value of β as given in table 1. See also figures 5 and 6.

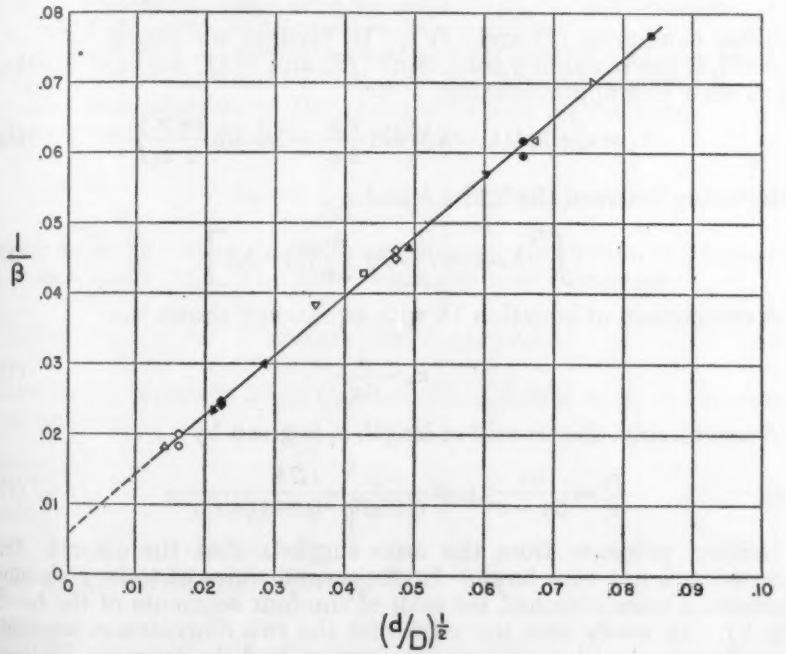


FIGURE 8.—*The reciprocal of β as a function of the square root of the curvature ratio d/D.*

The points represent the values of $1/\beta$ given in table 1, and the line represents the empirical equation $1/\beta=0.0050+0.844(d/D)^{1/2}$.

Reynolds number, on the other hand, must be small enough so that the flow would remain viscous, a very viscous liquid would be required.

In the absence of experimental information, we may resort to a simple computation, first to obtain an approximate value for x_1, and second, to establish a basis for the correct expression for x_1 in case experimental results become available. It is assumed in the following computation that x_1 is independent of the Reynolds number.

Assume that λ_a, the resistance coefficient at any arbitrary point of the transition segment, has no discontinuities, no maxima and no minima in the interval $0<x<x_1$.

The end conditions are:

$$\lambda_a=\lambda_s \text{ at } x=0, \quad (I)$$

$$\lambda_a=\lambda_c \text{ at } x=x_1, \quad (II)$$

$$\frac{d}{dx}(\lambda_a)=0 \text{ at } x=0, \quad (III), \text{ and}$$

$$\frac{d}{dx}(\lambda_a)=0 \text{ at } x=x_1 \quad (IV)$$

A polynomial representation of λ_a in circular functions satisfying the end conditions will give a first approximation of the values of λ_a. The expression

$$\lambda_a=\lambda_s+(\lambda_c-\lambda_s)\left(a_1 \sin \frac{\pi}{2}\frac{x}{x_1}+a_3 \sin \frac{3\pi}{2}\frac{x}{x_1}\right)$$

satisfies conditions (I) and (IV). If, further, we put $a_1=3/4$, and $a_3=-1/4$, the remaining conditions (II) and (III) are also satisfied. Thus, as a first approximation:

$$\lambda_a=\lambda_s+3/4(\lambda_c-\lambda_s)\left(\sin \frac{\pi}{2}\frac{x}{x_1}-1/3 \sin \frac{3\pi}{2}\frac{x}{x_1}\right). \quad (14)$$

Integrating between the limits 0 and x_1,

$$\int_0^{x_1} \lambda_a dx=x_1\left[\lambda_s+\frac{4}{3\pi}(\lambda_c-\lambda_s)\right]. \quad (15)$$

A comparison of equation 15 with equation 8 shows that

$$k_x=\frac{4}{3\pi}, \quad (16)$$

and accordingly, the transition length x_1 is given by

$$\frac{x_1}{d}=\frac{3\pi}{3\pi-4}\cdot\beta=\frac{1.74}{0.0059+0.844(d/D)^{1/2}} \quad (17)$$

Indirect evidence from the tests suggests that the error in this expression is not very large. In the second series of tests, resistance coefficients were obtained for each of the four segments of the bends (fig. 2). In every case the values for the two downstream segments were the same, within experimental errors, and the averages for these two segments were taken as the bend coefficient, λ_c. For the bend with curvature ratio $d/D=4.97\times10^{-4}$, the coefficient for the second segment was equal to λ_c, while the coefficient for the first was considerably lower. The relative transition length x_1/d, therefore, was

something less than the relative length of the first segment, which was $x/d=88.4$. A computation from equation 17 gives in this case $x_1/d=66.9$.

For the bend with curvature ratio $d/D=2.62\times10^{-4}$, the resistance coefficient for the second segment was a very little below the bend coefficient λ_c. In this case the relative transition length must have been slightly greater than the relative length, $x/d=88.4$ of the first segment. The computation from equation 17 gives $x_1/d=88.8$.

These results indicate that, if experimental data become available, equation 14 will constitute a satisfactory starting point for a more accurate determination of λ_a and x_1.

3. RESISTANCE IN A STRAIGHT PIPE BELOW A BEND

Let λ_z designate the effective resistance coefficient in a segment of straight pipe downstream from a bend and of length z measured from the downstream end of the bend. As the velocity distribution at the entrance to the tangent, at $z=0$, is that prevailing in the end portion of the bend, a certain transition length z_1 is necessary before the velocity distribution characteristic of a long straight pipe can be established. The definition of the effective coefficient, λ_z, is

$$\frac{1}{\gamma}\Delta p=\lambda_z\frac{z}{d}\frac{U^2}{2g}, \tag{18}$$

where Δp is the pressure difference between the end of the bend and a point on the straight pipe at distance $z>z_1$ downstream. As z becomes very large, λ_z approaches λ_s as a limit.

The coefficient λ_z depends on the relative length of the segment z/d, on the curvature ratio d/D and on the Reynolds number R_e. The analysis is analogous to that adopted above for the bend. For the effective coefficient we have the relation

$$\lambda_z\cdot z=\int_0^{z_1}\lambda_a dz+\lambda_s(z-z_1), \tag{19}$$

where λ_a is the resistance coefficient at any point within the transition segment, and $z>z_1$. The definite integral may be written

$$\int_0^{z_1}\lambda_a dz=\lambda_s z_1+k_z(\lambda_c-\lambda_s)z_1. \tag{20}$$

Substituting equation 20 in equation 19, dividing by d, and rearranging, we have

$$\frac{\frac{\lambda_z}{\lambda_s}-1}{\frac{\lambda_c}{\lambda_s}-1}\cdot\frac{z}{d}=k_z\frac{z_1}{d}\equiv Z, \tag{21}$$

where, for convenience, we write

$$Z\equiv k_z\frac{z_1}{d}. \tag{22}$$

The dimensionless quantity Z may be computed from equation 21 if the resistance coefficients λ_z, λ_c, and λ_s are known. λ_s is known when the Reynolds number is given, and λ_c can then be obtained from figure 4. It remains to determine λ_z.

Values of λ_z for a relative length of $z/d=215$ were determined with the experimental setup for the series *I* tests at the same time that the bends were tested. The results are shown in figures 9 and 10, where the ratio λ_z/λ_s is plotted as a function of the Reynolds number.

To determine Z, tentative curves were drawn to fit the experimental points in figures 9 and 10. About a dozen values of λ_z/λ_s were read from

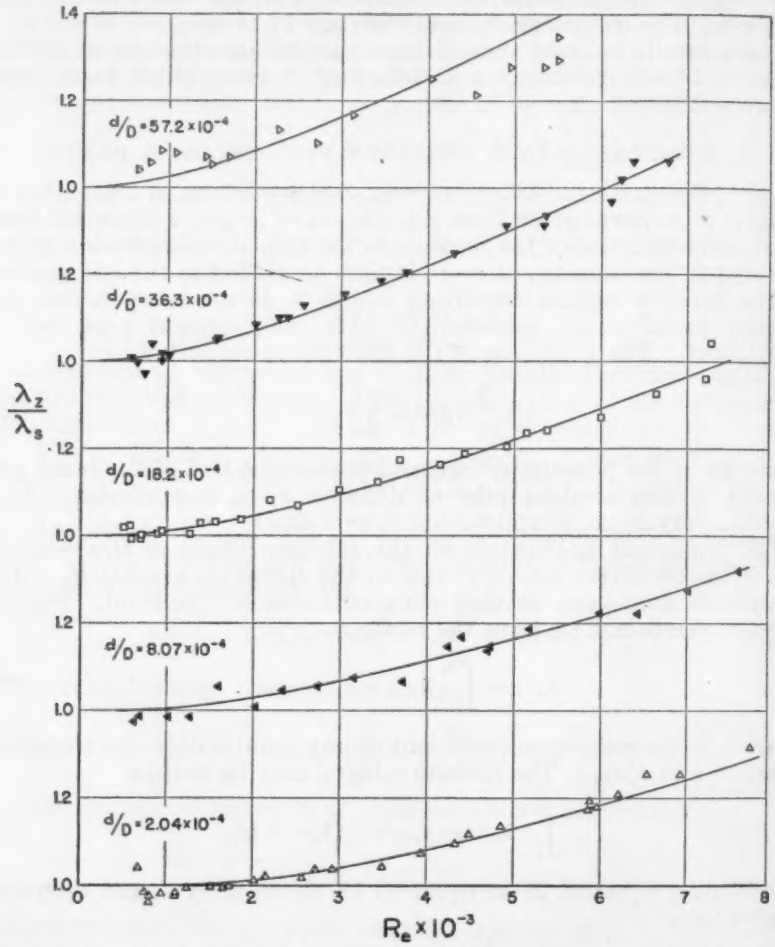


FIGURE 9.—*Ratio of the effective coefficient, λ_z, of the downstream tangent of relative length $z/d=215$, to the straight pipe coefficient, λ_s, as a function of Reynolds number.*

The points represent experimental values and each curve represents a constant value of ϕ as given in table 2. See also figure 10.

each curve, and corresponding values of λ_c/λ_s were found from the curve in figure 4. Then Z was computed from equation 21. A study of the results showed that they could be expressed in the form

$$Z=\left(\frac{\lambda_c}{\lambda_s}-1\right).\phi, \tag{23}$$

where ϕ was a constant for each bend, that is, ϕ is a function of d/D, but not of R_e.

In comparing the quantity Z as given by equation 23, with the analogous quantity β in equation 12, it should be noticed that β is independent of the Reynolds number and is a function of d/D only, because the velocity distribution at the entrance to the bend is always parabolic, whereas at the entrance to the downstream tangent the velocity distribution depends on the flow in the bend, which is a func-

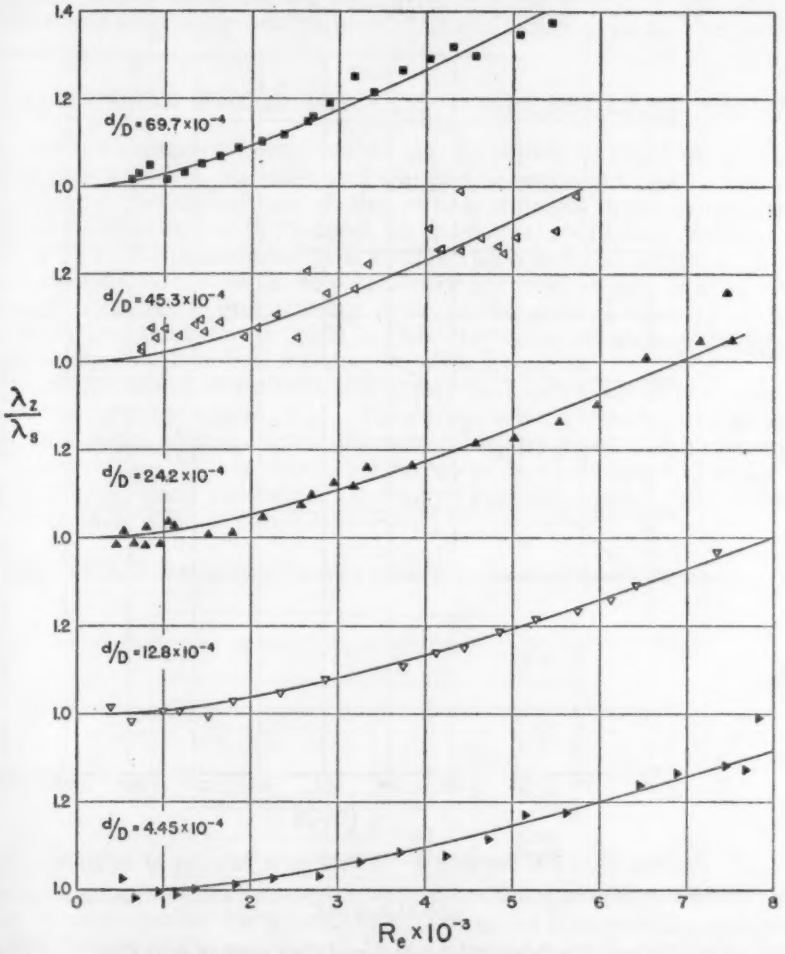


FIGURE 10.—*Ratio of the effective coefficient, λ_z, of the downstream tangent of relative length $z/d=215$, to the straight pipe coefficient, λ_s, as a function of Reynolds number:*

The points represent experimental values and each curve represents a constant value of ϕ as given in table 2. See also figure 9.

tion of both the Reynolds number and d/D. The curves drawn in figures 9 and 10 represent the final values adopted for ϕ as given in table 2. They appear to fit the data better than did the original tentative curves. The agreement is quite satisfactory in most cases, proving that ϕ is independent of Reynolds number within the errors of observation.

An empirical relation between ϕ and the curvature ratio d/D was found by plotting $\phi^{1/2}(d/D)^{1/2}$ as a function of $(d/D)^{1/2}$, as in figure 11. The straight line representing the points is given by the equation

$$\phi^{1/2}(d/D)^{1/2}=0.141+4.50(d/D)^{1/2}. \tag{24}$$

Hence,

$$\phi=[0.141\ (d/D)^{-1/2}+4.50]^2. \tag{25}$$

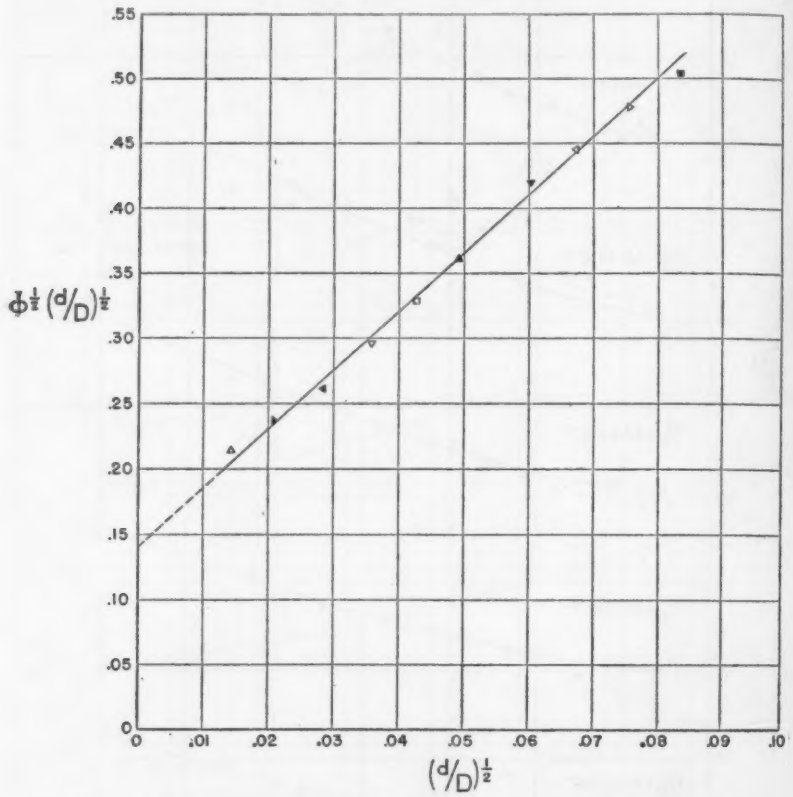


FIGURE 11.—*The quantity* $\phi^{1/2}(d/D)^{1/2}$ *as a function of* $(d/D)^{1/2}$.

The points represent the values given in table 2, and the line represents the empirical equation $\phi^{1/2}(d/D)^{1/2}=0.141+4.50\ (d/D)^{1/2}$.

TABLE 2.—*Relation between* ϕ *and the curvature ratio* d/D

d	z/d	$(d/D)\times10^4$	$(d/D)^{1/2}\times10^2$	$\phi\times10^{-2}$	$\phi^{1/2}(d/D)^{1/2}$
0.950	215.0	2.04	1.43	2.23	0.214
		4.45	2.12	1.25	.237
		8.07	2.84	.838	.261
		12.8	3.58	.685	.296
		18.2	4.27	.588	.329
		24.2	4.92	.535	.361
		36.3	6.03	.485	.420
		45.3	6.73	.434	.445
		57.2	7.56	.400	.478
		69.7	8.35	.365	.504

Finally, combining equations 22, 23, and 25, we have

$$\lambda_z = \lambda_s + \frac{d}{z}[0.141(d/D)^{-1/2} + 4.50]^2 \frac{(\lambda_c - \lambda_s)^2}{\lambda_s}, \tag{26}$$

which gives the effective coefficient of resistance for a downstream tangent of length $z > z_1$.

A computation of z_1, similar to that of x_1 given above, would be of little interest since only one value of z, much larger than z_1, was used in the tests.

V. TRANSITION FROM VISCOUS TO TURBULENT FLOW

The critical number is defined as the Reynolds number at which viscous flow becomes unstable and changes to turbulent flow. For a straight pipe the magnitude of the critical number depends on the entrance conditions, and for a bend, on the curvature ratio d/D also.

If the flow at the entrance to a straight pipe is made turbulent by introducing disturbances in any arbitrary manner, it will change to viscous flow at some downstream point in the pipe if the Reynolds number is less than about 2,200. This Reynolds number (2,200) is known as the lower critical number for straight pipe.

There is likewise a lower critical number for a bend, which is a function of the curvature ratio, d/D. This lower critical number starts at 2,200 for a bend of zero curvature ratio (straight pipe) and increases as d/D increases. This is shown by the lower curve in figure 12 which is drawn to fit data published by several experimenters. The data themselves are given in table 3.

TABLE 3.—*Critical number for pipe bends with disturbed flow at entrance*

Author	$d/D \times 10^4$	Critical number
White	4.89	2,250
Do	200.	6,000
Do	660.	9,000
Adler	50.	3,980
Do	100.	4,730
Do	200.	5,620
Taylor	310.	6,350
Do	540.	7,100

The critical number for a straight pipe may be increased by reducing disturbances at the entrance. In the present tests, for example, it was raised to 9,200 by the use of the special bell-mouth entrance shown in figure 3. So long, therefore, as the Reynolds number was less than 9,200, the flow at the entrance to the bend was viscous. Under these entrance conditions, the critical numbers given in table 4 were found for the bend. These values are plotted in figure 12 (upper curve).

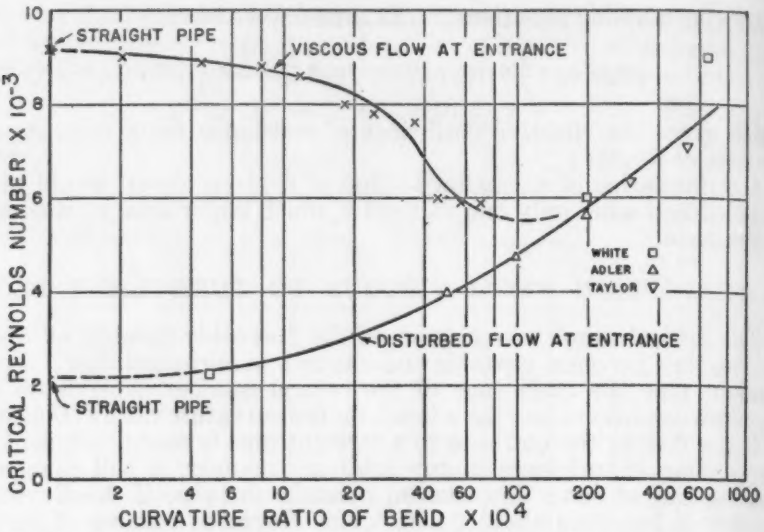


FIGURE 12.—*Critical numbers for bends as function of the curvature ratio.*

The crosses represent values given in table 4, and the other points values given in table 3.

TABLE 4.—*Critical number for pipe bends with laminar flow at entrance*

$(d/D)\times10^4$	Central angle α	Critical number
	Degrees	
0.00	0	9,200
2.04	5	9,000
4.45	10	8,900
8.07	20	8,800
12.8	30	8,600
18.2	45	8,000
24.2	60	7,800
36.3	90	7,600
45.3	120	6,000
57.2	150	5,900
69.7	180	5,900

As it was not convenient to determine these critical numbers with any certainty by direct observations of the bend loss on the bends themselves, they were determined indirectly by observations on the straight pipe downstream. If the Reynolds number was less than 9,200, any change from viscous to turbulent flow in this downstream pipe could be due only to turbulent flow in the bend. Hence, the downstream tangent forms a convenient detector of turbulence in the bend. The critical numbers given in table 4 were determined by inspection from the right-hand diagrams of figures 13, 14, and 15.

It will be noticed from figure 12 that as the curvature ratio increases, the critical number decreases and approaches the values for bends with disturbed flow at entrance at a value of the curvature ratio somewhat greater than 0.01.

In figures 13, 14, and 15, the resistance coefficients for pipes no. 1 and no. 2 are plotted against Reynolds number in the region of change from viscous to turbulent flow. For the bends, however, there is no

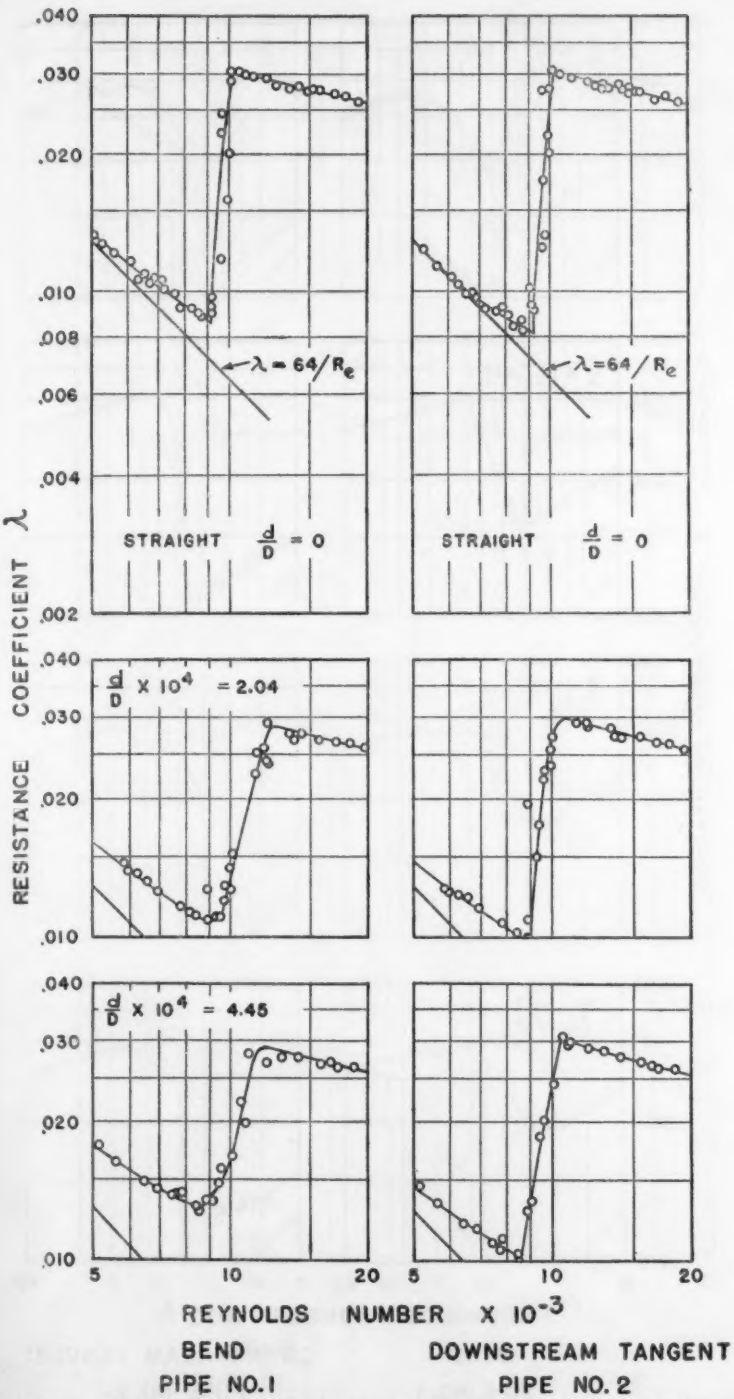


FIGURE 13.—*Resistance coefficients in the critical region for bends and downstream tangents as functions of Reynolds number.*

See also figures 14 and 15.

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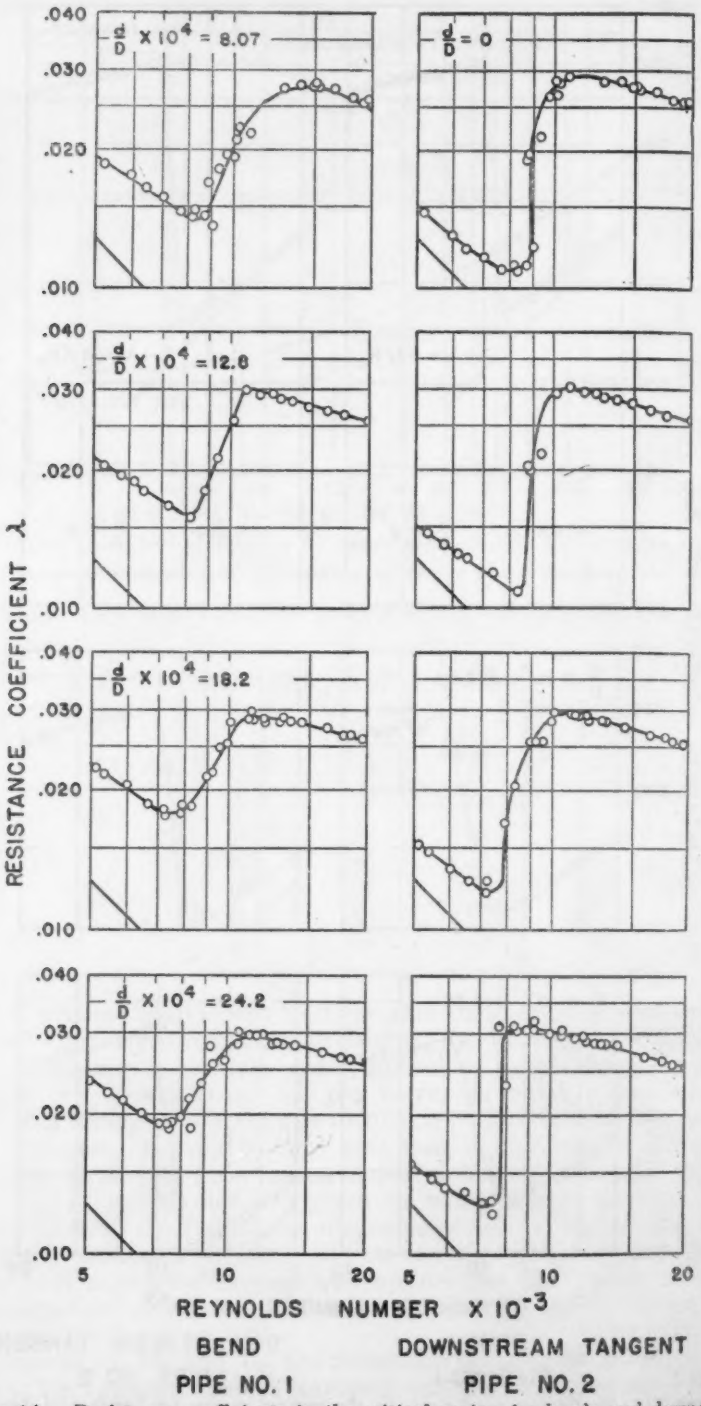

FIGURE 14.—*Resistance coefficients in the critical region for bends and downstream tangents as functions of Reynolds number.*

See also figures 13 and 15.

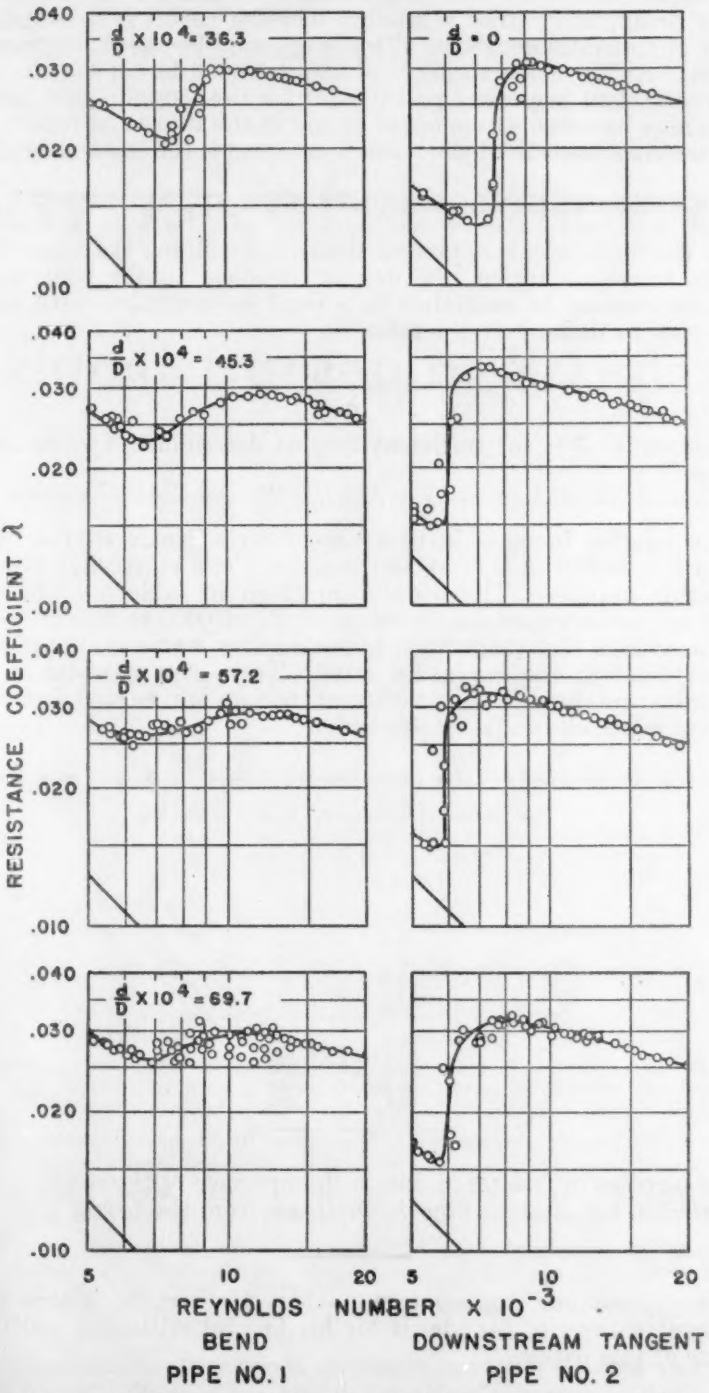

FIGURE 15.—*Resistance coefficients in the critical region for bends and downstream tangents as functions of Reynolds number.*

See also figures 13 and 14.

sharp break, but rather a gradual increase covering a considerable range of Reynolds numbers. This range may be called the transition region. At Reynolds numbers of about 10,000 to 13,000, the resistance coefficient becomes equal to that for the straight pipe, and this point may be taken as the upper bound of the transition region. The characteristic feature of the transition region is the instability of flow.

VI. EXPERIMENTAL RESULTS FOR TURBULENT FLOW

At Reynolds numbers greater than that defining the upper bound of the transition region, the flow is turbulent in the bend and the relative increase in resistance in a bend as compared with straight pipe may be defined by the ratio

$$\frac{\lambda_c-\lambda_s}{\lambda_s}.$$

The value of λ_s for turbulent flow as determined by this investigation is

$$\lambda_s=0.309R_e^{-1/4}.$$

The relative increase in resistance for the bends studied (in the range R_e=40,000 to R_e=60,000) was small and varied but little with Reynolds number. The results are given in table 5. The values given are mean values for the range of R_e=40,000 to R_e=60,000. It will be noticed that the relative increase in resistance is approximately proportional to the curvature ratio. Tests over a wider range of Reynolds numbers in the turbulent region are needed before any definite relations can be established.

TABLE 5.—*Relative increase in resistance for turbulent flow in pipe bends*

[Mean values for the range R_e=40,000 to R_e=60,000]

$d/D\times10^4$	$\frac{\lambda_c-\lambda_s}{\lambda_s}$
2.04	0.010
4.45	.006
8.07	.011
12.8	.010
18.2	.017
24.2	.028
36.3	.042
45.3	.058
57.2	.057
69.7	.073

No increase in resistance due to the presence of the bends could be detected in the straight pipe downstream from the bends.

We express our appreciation to Mr. Herbert N. Eaton of the National Bureau of Standards for his helpful criticisms and careful review of this paper.

WASHINGTON, October 19, 1936.